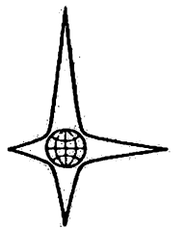
V. Alexeyev

QUALITATIVE ANALYSIS



MIR
PUBLISHERS

В. Н. АЛЕКСЕЕВ

КАЧЕСТВЕННЫЙ АНАЛИЗ

ИЗДАТЕЛЬСТВО
«ХИМИЯ»
МОСКВА

V. N. ALEXEYEV

QUALITATIVE ANALYSIS

Translated from the Russian
by
E. B. UVAROV

MIR PUBLISHERS
MOSCOW 1967

This work is a textbook for a course of qualitative chemical analysis. It presents the theoretical principles of qualitative analysis, and describes the most important reactions of various anions and cations and systematic procedures for analysis of their mixtures. Certain spot and microchemical tests for detection of cations and anions are examined. Special chapters deal with the detection of titanium, vanadium, molybdenum and tungsten ions and with the analysis of metals and alloys.

The book is intended for students in non-chemical institutions of higher education.

Revised from the Russian 1959 Edition

На английском языке

CONTENTS

Chapter I. **Introduction**

1. **The subject and methods of analytical chemistry** 11
2. **Methods of carrying out analytical reactions** 15
3. **Microcrystalloscopic reactions** 18
4. **Concentration of reagent solutions** 21
5. **Reaction conditions. Sensitivity and specificity of reactions** . . . 24
6. **Fractional and systematic analysis** 28
7. **Classification of cations in qualitative analysis. Group reagents** 30
8. **Brief historical review of the development of analytical chemistry** 36

Questions and problems 41

Chapter II. **Cations of Group I**

Theoretical aspects

9. **The law of mass action** 43
10. **Degree of dissociation. Strong and weak electrolytes** 48
11. **Dissociation constants of weak electrolytes** 52
12. **Shift of ionic equilibria. The common ion effect** 57
13. **The state of strong electrolytes in solution** 60
14. **Activity. Activity coefficient** 63
15. **Dissociation of water. The hydrogen ion exponent (pH)** 67
16. **Buffer systems** 72
17. **Determination of pH in the course of qualitative analysis** 79

Questions and problems 83

Reactions and analytical procedure for Group I cations

18. **General characteristics of Group I cations** 85
19. **Reactions of the K^+ cation** 86
20. **Reactions of the Na^+ cation** 91
21. **Reactions of the NH_4^+ cation** 94

22. Reactions of the Mg^{++} cation 99
23. Analysis of mixtures of Group I cations 104

Questions and problems 110

Chapter III. Cations of Group II

Theoretical aspects

24. Solubility product 111
25. Influence of common ions on solubility. The salt effect . 117
26. Formation of precipitates 122
27. Fractional precipitation 134
28. Dissolution of precipitates 135
29. Interconversion of sparingly soluble electrolytes 139
30. Direction of exchange reactions 144
31. Modern views on the nature of acids and bases 146

Questions and problems 151

Reactions and analytical procedure for Group II cations

32. General characteristics of Group II cations 153
33. Action of the group reagent 155
34. Techniques of separation reactions 158
35. Reactions of the Ba^{++} cation 163
36. Reactions of the Sr^{++} cation 166
37. Reactions of the Ca^{++} cation 168
38. Analysis of mixtures of Group II cations 170

Questions and problems 178

Chapter IV. Cations of Group III

Theoretical aspects

39. Precipitation of sulphides 180
40. Action of acids on sulphides 184
41. Colloidal systems 189
42. Coprecipitation 195

Questions and problems 198

43. Hydrolysis of salts 199
44. Degree of hydrolysis and the pH of salt solutions 208
45. Amphoteric compounds 217

Questions and problems 223

46. Double and complex salts 224
47. Structure of complex compounds 226
48. Stability of complexes 230
49. Significance of complex compounds in analysis 235
50. Oxidation-reduction reactions 240

Questions and problems 251

Reactions and analytical procedure for Group III cations

51. General characteristics of Group III cations 254
52. Action of the group reagent 258
53. Reactions of the Al^{+++} cation 263
54. Reactions of chromium ions 269
55. Reactions of iron cations 275
56. Reactions of the Mn^{++} cation 279
57. Reactions of the Zn^{++} cation 285
58. Reactions of the Co^{++} cation 290
59. Reactions of the Ni^{++} cation 294
60. Analysis of mixtures of Group III cations 296

Questions and problems 315

Chapter V. **Cations of Group IV**

Theoretical aspects

61. Oxidation potentials 317
62. Direction of oxidation-reduction reactions 324
63. Influence of concentration and of the reaction of the medium 329
64. Equilibrium constants of oxidation-reduction reactions 332

Questions and problems 339

Reactions and analytical procedure for Group IV cations

65. General characteristics of Group IV cations 340
66. Action of the group reagents 343
67. Reactions of the Ag^{+} cation 349
68. Reactions of the Pb^{++} cation 352
69. Reactions of mercury cations 354
70. Reactions of the Cu^{++} cation 356
71. Reactions of the Cd^{++} cation 359
72. Reactions of the Bi^{+++} cation 362
73. Analysis of mixtures of Group IV cations 366

Questions and problems 377

Chapter VI. Cations of Group V

74. General characteristics of Group V cations. Thiosalts 379
75. Action of the group reagent 384
76. Reactions of arsenic ions 389
77. Reactions of antimony ions 393
78. Reactions of tin ions 397
79. Analysis of mixtures of Group V ions 401
80. Qualitative analysis of cations without use of hydrogen sulphide 410

Questions and problems 413

Chapter VII. The elements titanium, vanadium, molybdenum and tungsten

81. General characteristics 415
82. Reactions of the Ti^{++++} ion 418
83. Reactions of the VO_3^- ion 419
84. Reactions of the MoO_4^{--} ion 421
85. Reactions of the WO_4^{--} ion 422
86. Analysis of mixtures of the ions Ti^{++++}, VO_3^-, MoO_4^{--}, WO_4^{--} . . 423

Questions and problems 427

Chapter VIII. Anions

87. Classification of anions 428

First group of anions 428

88. Reactions of sulphate, SO_4^{--} 430
89. Reactions of sulphite, SO_3^{--} 431
90. Reactions of thiosulphate, $S_2O_3^{--}$ 434
91. Reactions of carbonate, CO_3^{--} 435
92. Reactions of phosphate, PO_4^{---} 437
93. Reactions of borate ions, $B_4O_7^{--}$ and BO_2^- 440
94. Reactions of fluoride, F^- 441
95. Reactions of silicate, SiO_3^{--} 443
96. Reactions of oxalate, $C_2O_4^{--}$ 445

Second group of anions 447

97. Reactions of chloride, Cl^- 447
98. Reactions of bromide, Br^- 451
99. Reactions of iodide, I^- 452
100. Reactions of sulphide, S^{--} 456
101. Reactions of thiocyanate, CNS^- 459
102. Reactions of ferrocyanide, $[Fe(CN)_6]^{=}$ 462
103. Reactions of ferricyanide, $[Fe(CN)_6]^{---}$ 464
104. Analysis of mixtures of Group II anions 466

Third group of anions 469

105. Reactions of nitrate, NO_3^- 469
106. Reactions of nitrite, NO_2^- 472
107. Reactions of acetate, CH_3COO^- 474
108. Reactions of permanganate, MnO_4^- 475
109. Analysis of mixtures of anion Groups I, II and III 476

Questions and problems 483

Chapter IX. **General course of analysis (detection of cations and anions)**

110. Preliminary observations and preparation of the substance for analysis 485
111. Preliminary tests 486
112. Detection of cations 490
113. Detection of cations in presence of the phosphate anion 498
114. Detection of anions 503
115. Analysis of metals and alloys 506

Questions and problems 514

Chapter X. **Brief information on spot tests**

116. General characteristics of the spot test method 515
117. Spot tests for individual cations 517

Appendices 530

I. Reagents used in qualitative analysis 530
II. Degrees of dissociation of acids, bases and salts in aqueous solutions at 18° 538
III. Dissociation constants and exponents (pK) of some weak electrolytes 540

IV. Solubilities and solubility products of certain sparingly soluble electrolytes at room temperature 542
V. Instability constants of certain complexes 544
VI. Preparation of buffer mixtures 545
VII. Indicators for pH determination 546
VIII. Standard oxidation potentials 548
IX. Atomic weights of certain elements 549
Name Index 551
Subject Index 553

CHAPTER I

INTRODUCTION

1. The Subject and Methods of Analytical Chemistry

The task of analytical chemistry is to develop and provide a theoretical basis for methods of chemical analysis, used for determining the chemical composition of substances or mixtures. In analytical operations, first the qualitative composition of the substance is determined, i.e., it is found what elements or ions are present in it. Then the quantitative composition is found, i.e., the quantitative proportions of these elements or ions in the substance are determined.

The purpose of *qualitative analysis* is to discover or "detect" individual elements or ions present in a substance.

Determination of the amounts of the individual components of a substance is the primary objective of *quantitative analysis.*

It is obvious that qualitative analysis should precede quantitative analysis. Qualitative analysis has to be resorted to even when it is necessary to determine the percentage content of a certain component known to be present in a given substance. This is because the most suitable method for quantitative determination of the particular component can be selected only when it is known what other elements or ions are present.

Analytical chemistry, and in particular qualitative analysis, is of enormous scientific and practical importance, being one of the most important methods for investigating substances and their changes. It also plays a most important part in branches of science allied to chemistry—mineralogy, geology, physiology and microbiology, as well as in medicine, agriculture and technology.

The investigator has to use the methods of analytical chemistry in almost every scientific investigation concerned in one way or another with chemical phenomena. Its applied uses are no less important. Chemical analysis is of considerable significance in the national economy; it is indispensable for chemical control of production in the most important branches of industry, for chemical investigation of soils, fertilizers, agricultural products, useful minerals, etc.

A variety of methods, chemical, physical, and physico-chemical, can be used for qualitative analysis, i.e., for detection of elements or

ions contained in a given substance. (The same is true of quantitative analysis.)

In *chemical methods* of qualitative analysis the element or ion to be detected is converted into some new compound which has specific properties on the basis of which its formation can be elucidated. The chemical change taking place is known as an *analytical reaction* and the substance causing it is a *reagent.*

A distinction is made between macro-, micro-, semimicro- and ultramicro-methods of qualitative analysis, dependent on the amounts of substances used for the analytical reactions.

In *macroanalysis* relatively large amounts of substance (0.5-1 g) or solution (20-50 ml) are used. The reactions are carried out in ordinary test tubes (10-20 ml), beakers or flasks. Precipitates are separated from solutions by filtration through paper filters.

The amount of substance used in *microanalysis* is usually about 1/100 of the amount involved in macroanalysis work, i.e., a few milligrams of solid or some tenths of a millilitre of solution. Highly sensitive reactions are used, which make it possible to detect the individual components even when they are present in small amounts. These reactions are carried out either by the *microcrystalloscopic* or by the *drop method.*

In the *microcrystalloscopic* method the reactions are usually carried out on a glass *microscope slide* and the presence of a given ion or element is deduced from the form of the crystals formed, which are examined under the microscope.

Drop reactions or *spot tests* are reactions accompanied by a change of colour of solutions or by formation of coloured precipitates. The tests are most commonly performed on strips of filter paper; drops of the unknown solution and of the reagents are applied to it in a definite sequence. The reaction produces a coloured spot on the paper, indicating the presence of a particular ion in the unknown solution. These tests can also be carried out on special spot plates with numerous depressions, on watch-glasses, in porcelain crucibles, etc.

Semimicroanalysis occupies an intermediate position between the macro- and micro-methods. The amount of substance used in this method is about 1/20-1/25 of the amount used in macroanalysis, which corresponds to about 50 mg of solid or 1 ml of solution.

Semimicroanalysis has a number of advantages over macroanalysis, and gives equally reliable results with careful working.

Ultramicroanalysis is used for investigation of less than 1 mg of substance. The various analytical operations are performed under the microscope.

The differences in technique in the different methods of analysis are shown schematically in Fig. 1, where the different ways of separating precipitates from solutions are compared.

Chemical methods of analysis, like any other experimental methods, have a limited field of applicability outside which they are unsuitable. For example, the existing methods do not always satisfy the increasingly stringent demands of science and technology with regard to sensitivity, i.e., to suitability for detecting and determining "traces" (very small amounts) of various impurities. The speed of analysis by chemical methods is also sometimes inadequate for industrial needs, as it is very essential in industry to obtain analytical results in time to regulate the process in order to prevent production of substandard material.

For this reason physical and physico-chemical methods of analysis, which are preferable in some cases to chemical methods, are being increasingly used.

Physical methods of analysis are based on the relationships between the chemical composition and certain physical properties of substances. They include *spectrum analysis* based on investigation of the emission spectra produced by substances in a burner flame, electric arc, etc. Spectral lines corresponding to certain wavelengths characteristic of various elements indicate the presence of these elements, while the quantitative contents are estimated from the line intensities.

The spectrum method is highly sensitive (about 10^{-6}-10^{-8} g of some elements can be detected) and requires little time and small amounts of substance.

We should also mention *luminescence analysis* based on observations of the luminescence emitted when a substance is irradiated by ultraviolet rays. The source of these rays is a mercury quartz lamp with a light filter to stop visible radiation. Luminescence analysis is even more sensitive than spectrum analysis (down to 10^{-10} g of substance can be detected). However, only some substances exhibit luminescence, and this greatly restricts the applicability of the method. Despite this, it is successfully used in a number of branches of science and technology (in analysis of minerals and organic compounds, in biology, medicine and agriculture, in investigations of food products and tanning agents, for grading glasses, in studies of oil wells, etc.).

Among the physico-chemical methods used in qualitative analysis we must first mention the *chromatographic method.* In this method the unknown solution is passed through a glass column containing a solid powdered adsorbent (for example, Al_2O_3). Since the adsorption* of different substances or ions differs greatly, they become separated and can be detected in the column either by their character-

* Adsorption is a process in which ions or molecules of a substance are concentrated from the surroundings in the surface layer of another substance.

istic colours or by treatment with reagents which form differently coloured compounds with them.

Next, we note the *polarographic method* in which the solution is electrolyzed with a dropping mercury cathode in a special instrument (polarograph). The instrument automatically records the so-called volt-ampere curve which shows the variations of current strength with increasing voltage. This curve can be used not only for qualitative detection of the cations present, but also for their quantitative determination. The method is highly sensitive and takes very little time. It is very suitable for determination of trace impurities in metals, alloys, and similar materials.

Mention should also be made of the *tracer-atom method of analysis*, by the use of radioactive isotopes of the elements to be determined, and of the *radioactivation method* based on the formation of radioactive isotopes (or new elements) when the substance is irradiated by elementary particles. These methods are not considered further in this book.

Because of these specific characteristics of physical and physicochemical methods, they are becoming increasingly important in analytical practice. However, chemical methods (which are also advancing rapidly) continue to play the leading part. They are also the most important in the study of analytical chemistry.

This book is concerned with methods of inorganic analysis only. Organic substances are investigated by other methods, the most important of which are described in special manuals.

2. Methods of Carrying Out Analytical Reactions

Analytical reactions can be carried out by "dry" and "wet" methods.

In the former case the unknown substance and the appropriate reagent are taken in the solid state and are usually heated together to a high temperature; in the latter case the interaction between the substance and the appropriate reagent in solution is observed.

Dry reactions include tests based on *flame colouration* by salts of certain metals. For example, when sodium salts are introduced on platinum wire into a non-luminous gas flame they colour the flame intense yellow; potassium salts give a lilac colour, strontium—crimson, barium—green, etc. Under suitable conditions the presence of these elements in unknown substances can be detected by these colours.

Dry reactions also include the formation of *coloured beads* (glasses) of sodium tetraborate (borax), $Na_2B_4O_7 \cdot 10H_2O$, or of sodium-ammonium hydrogen phosphate ("microcosmic salt"), $NaNH_4HPO_4 \cdot 4H_2O$, when they are fused with the salts of certain metals, and

the *fusion* of unknown substances with various "fluxes" such as mixtures of solid Na_2CO_3 and K_2CO_3, or Na_2CO_3 and KNO_3, etc.

These methods, known as *pyrochemical*, are widely used in analysis of minerals and rocks.

Grinding of an unknown solid substance with a solid reagent is another method which is sometimes used. This method, proposed in 1898 by F. M. Flavitsky (1848-1917) is based on the formation of coloured compounds of the elements being detected. For example, to detect cobalt a few crystals of the solid, such as $CoSO_4$, are rubbed on a porcelain plate with an approximately equal amount of a solid reagent, in this case ammonium thiocyanate, NH_4CNS. The mixture becomes blue owing to the formation of a complex cobalt salt, $(NH_4)_2[Co(CNS)_4]$. The reaction is represented by the equation

$$CoSO_4 + 4NH_4CNS = (NH_4)_2[Co(CNS)_4] + (NH_4)_2SO_4$$

These reactions can be carried out with very small amounts of material.

It should be pointed out that most reactions which take place during grinding of solids proceed with the aid of water adsorbed from the air, so that they are not really "dry" reactions.

Dry reactions play a subsidiary part, and are generally used as preliminary tests.

Reactions carried out by the wet method, i.e., between substances in solutions, are most often used in qualitative analysis. For these reactions to proceed the substance under test must first be dissolved. The usual solvent is water, or an acid if the substance is insoluble in water. In the latter case the substance is converted into some salt readily soluble in water, for example:

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$
$$Fe(OH)_3 + 3HCl = FeCl_3 + 3H_2O$$
$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2\uparrow \text{ *}$$

In qualitative analysis use is made of only the reactions accompanied by *external effects* or easily recognized changes which indicate that they have actually taken place. The usual external effects are:

(a) a change in the colour of the solution;

(b) formation (or dissolution) of a precipitate;

(c) evolution of gases.

Reactions accompanied by formation of precipitates and changes of solution colour are most commonly used.

---

* An upward arrow indicates that the substance is given off as a gas; a downward arrow indicates precipitation.

In most cases analysis of inorganic substances involves the use of aqueous solutions of salts, acids or bases. These substances are electrolytes, i.e., they are dissociated into ions in aqueous solutions. Therefore *wet reactions usually take place between free ions, and in using these reactions we detect the ions formed by elements, and not the elements themselves**.

For example, chlorine is detected in HCl or in chloride solutions by the action of silver nitrate solution, $AgNO_3$. A characteristic curdy white precipitate of AgCl is formed, and this is taken as an indication of the presence of chlorine:

$$HCl + AgNO_3 = \downarrow AgCl + HNO_3$$

$$CaCl_2 + 2AgNO_3 = \downarrow 2AgCl + Ca(NO_3)_2, \text{ etc.}$$

In these equations all the salts, with the exception of the precipitated AgCl, are present in solution as the respective ions. Accordingly, the last reaction may be written in the following form:

$$Ca^{++} + 2Cl^- + 2Ag^+ + 2NO_3^- = \downarrow 2AgCl + Ca^{++} + 2NO_3^-$$

Since the Ca^{++} and NO_3^- ions remain unchanged, their presence is of no significance in the reaction; therefore they may be omitted from the equation. We therefore have:

$$2Cl^- + 2Ag^+ = \downarrow 2AgCl$$

or (after dividing through by 2)

$$Cl^- + Ag^+ = \downarrow AgCl$$

This is the *ionic equation* for the reaction. The same ionic equation is obtained for any other reaction between a chloride in solution and $AgNO_3$.

The ionic equation shows that *the reaction essentially consists of the interaction of* Ag^+ *and* Cl^- *ions present in the solution to form the precipitate of* AgCl. If chlorine is present not in the form of Cl^- ions but as some other ions (such as chlorate, ClO_3^-) or undissociated molecules (e.g., chloroform, $CHCl_3$), this reaction does not occur. In fact, although substances such as $KClO_3$ or $CHCl_3$ contain the element chlorine, AgCl is not precipitated by the action of silver nitrate on them. Therefore it is evident that in using this reaction we detect the Cl^- ion and not the element chlorine. In the same way, the reagent for the Cl^- ion is not $AgNO_3$ but the Ag^+ ion present

* Of course, when a particular ion has been found, the presence of the corresponding element in the substance can be inferred.

in solution. It is therefore possible to use solutions of Ag_2SO_4, CH_3COOAg, etc., instead of $AgNO_3$:

$$2NaCl + Ag_2SO_4 = \downarrow 2AgCl + Na_2SO_4$$

$$CaCl_2 + 2CH_3COOAg = \downarrow 2AgCl + (CH_3COO)_2Ca$$

If the element forms ions of different valencies, each gives its own characteristic reactions. For example, the Fe^{+++} ion forms a reddish-brown precipitate of $Fe(OH)_3$ by the action of alkalies (i.e., OH^- ions), whereas the Fe^{++} ion gives a dingy green precipitate of $Fe(OH)_2$ with alkalies. In the same way, the Cu^{++} and Cu^+ ions, the MnO_4^- and MnO_4^{--} ions, etc., give different reactions. Therefore the valencies of elements in the substances being analyzed are usually established by qualitative analysis.

Since wet reactions detect ions and not elements, it is possible in analysis of individual substances to establish their formulas during the qualitative tests. For example, if we detect Na^+ and Cl^- ions by the appropriate reactions and find no other ions in the unknown substance, we can obviously conclude that the substance is sodium chloride, NaCl. Similarly, if we find only Fe^{+++} and SO_4^{--} ions or Fe^{++} and SO_4^{--} ions, we can assume that the formula of the substance is $Fe_2(SO_4)_3$ or $FeSO_4$, respectively, etc. On the other hand, quantitative as well as qualitative analysis is needed to establish even the empirical formula of an organic compound which does not dissociate into ions*. Thus, compounds which undergo electrolytic dissociation are much easier to analyze than those which do not dissociate.

Electrolytic dissociation or ionization has also the following singificance in analytical chemistry. The number of the most important cations is relatively small, about 25. The number of the best-known anions is similar. The number of (neutral) salts which they form, however, exceeds 600. Since in solution all these salts are dissociated into ions, which are detected in analysis, to identify any of these salts we need know the reactions of only 50 ions. In the case of non-ionizing organic compounds ionic reactions cannot be used, and therefore each such substance has to be identified from all its physical and chemical properties, which is a much more difficult problem.

3. Microcrystalloscopic Reactions

In addition to macroreactions, in this book we also examine certain microcrystalloscopic and drop reactions (spot tests) for

* To establish the molecular formula it is also necessary to determine the molecular weight of the substance.

various ions. Since Chapter X is concerned with spot tests, we deal at this point with microcrystalloscopic reactions only.

The microscope was first used in chemical investigations in 1744, when the great Russian scientist M. V. Lomonosov used it for studying the reaction in which iron dissolves in nitric acid. Lomonosov was well aware of the significance of microscopic observations and used the microscope widely in a number of his subsequent investigations.

In 1798 another eminent Russian chemist, T. E. Lowitz, who made a number of important discoveries in the chemical field, drew attention to the fact that microcrystals of various salts, when observed under the microscope, have very characteristic shapes which can be used for identifying the salts.

Lowitz made about 100 drawings of various "salt deposits" and applied his discovery to analytical purposes. Thus, Lomonosov and Lowitz are the founders of microcrystalloscopic analysis. It was subsequently developed by P. N. Akhmatov, who published in 1873 a paper entitled *Application of the Microscope to Chemical Investigations.* He designed an instrument for measurement of crystal angles (goniometer) and used it for analytical purposes, and developed a number of microchemical methods for detection of various ions, including cations of analytical Groups I and II. However, it was not until later, in the 1890's, that microcrystalloscopic analysis became generally adopted. It was widely used by D. S. Belyankin, who published in 1905 a manual on microcrystalloscopic analysis of minerals and rocks.

The microcrystalloscopic method has been developed particularly widely in the USSR during the past 20 years. Many Soviet chemists are working successfully in this field of analytical chemistry.

By microscopic observations of the shapes of the crystals formed during chemical reactions it is usually possible to deduce rapidly and with certainty the presence of particular ions in the solution used.

It must be remembered, however, that crystals assume their characteristic form only under favourable crystallization conditions, among which fairly slow crystal growth is especially important. The required rate of growth is generally observed when crystallization proceeds from slightly supersaturated solutions. During the first few instants a relatively small number of minute crystal nuclei are formed; these gradually grow as the result of deposition of the appropriate ions on their surface and eventually attain a fairly large size. On the other hand, if crystallization proceeds in a strongly supersaturated solution, very numerous nuclei are formed at once, and these cannot become very large. Moreover, in rapid crystallization the individual ions do not have time to achieve correct

orientation in relation to neighbouring ions and as a result small crystals are formed, not very characteristic in form, often consisting of concretions known as dendrites (tree-like formations).

The degree of supersaturation depends primarily on the concentration of the given ion, and increases with that concentration. It follows that, to obtain good crystals, relatively dilute solutions should be used for the precipitation. Moreover, under given conditions the higher the solubility of the compound formed the less the supersaturation. It is therefore often useful to raise to some degree the solubility of the substance formed by addition of a suitable reagent. Although this lowers the sensitivity of the reaction, it improves the crystallization conditions. Usually the best way of ensuring slow crystal growth is to take one of the reacting substances in solid form. As the substance dissolves and diffuses slowly to the farther regions of the drop, there is time for growth of well-developed crystals, especially from the edges of the drop.

If both the reacting substances are in the dissolved state, it is preferable not to mix the solutions but to place drops of them side by side and connect them by means of a small fibre or glass thread: the dissolved substances will slowly diffuse from drop to drop. Slow evaporation of the drop favours slow crystallization, especially if the solubility of the substance is high.

In microcrystalloscopic tests it must be remembered that *the presence of impurities may alter completely the form of the crystals formed.*

The microcrystalloscopic test technique is usually very simple. The test is carried out on a microscopic slide, which is a rectangular glass plate (75 × 25 mm), under the conditions specified above. The crystals formed are examined under the microscope at relatively low magnification (×50-200); cover glasses* are generally not used.

The microscope (Fig. 2) consists of the tube *1* equipped with two lens systems; the upper, *2*, is known as the eyepiece, and the lower, *3*, is the objective.

The tube is moved in a vertical direction by means of the rack *4* movement. The microscope substage *5* is located under the tube. Light rays, reflected by a mirror under the substage, pass through an opening in the substage.

In work with the microscope the mirror is first adjusted so that the field of vision is well illuminated. Either daylight or artificial light may be used for this purpose. The slide with the specimen is put on the substage (*make sure that the underside of the slide is dry*) and

* Small square plates of thin glass used for covering drops examined under he microscope in biological work.

for work at low magnifications (× 70-120) the objective is adjusted to a distance of about 0.5 cm from the slide, the microscope being viewed from the side for the purpose.

Then, with the left eye at the eyepiece (the right eye should be kept open), the tube is raised *very slowly*, the knob being turned until the specimen can be seen quite clearly. If this position cannot be found, the tube is lowered again (viewing the microscope *from the side*) to a distance rather less than 0.5 cm between the objective and the slide, and then raised again with the eye at the eyepiece.

Never lower the tube while looking through the eyepiece, as this inevitably leads to wetting of the objective with the solution, which is very harmful to the objective. If a drop of the solution should touch the objective, it must be wiped at once with a soft dry rag.

For high magnifications (used very rarely in microcrystalloscopic tests) the specimen must be covered with a cover glass, and the objective adjusted to about 0.5 mm from the specimen before the tube is raised.

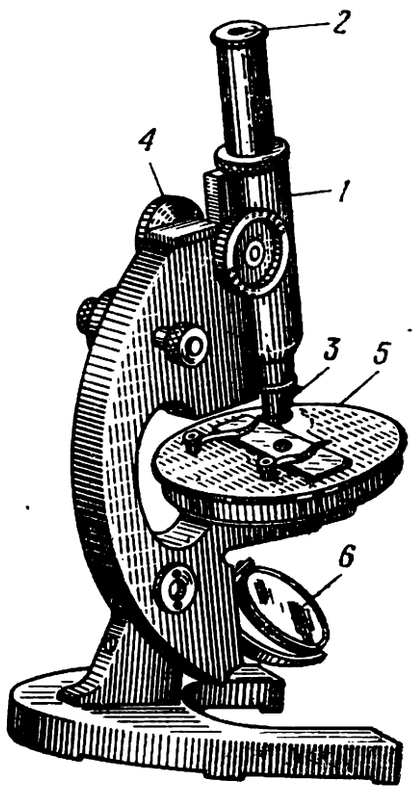


Fig. 2. Microscope
1—tube; *2*—eyepiece; *3*—objective; *4*—rack; *5*—substage; *6*—mirror

Microcrystalloscopic reactions are very sensitive in most cases. The detectable minimum (see Sec. 5) in these reactions is usually tenths or hundredths of a microgram, and in some instances as low as ten-thousandths of a microgram. Therefore clean and careful work is especially important in microcrystalloscopic tests. The reagents used must likewise conform to high standards of purity.

4. Concentration of Reagent Solutions

Wet-way reactions are in most cases performed in test tubes. To avoid waste, large volumes of the unknown solutions and therefore of the reagents should not be taken. The total volume of liquid should not be more than half the volume of the test tube. It must be remembered that a test carried out with 1-2 ml of solution is no less clear and convincing than one with 5-10 ml, and is considerably cheaper.

Beginners are often in doubt how much reagent to take for a particular test. Often they take too much and thus waste it. As will

be shown later, a large excess of reagent is quite often harmful as it causes the reaction to take an unwanted course.

To avoid such waste and complications, the solutions used in qualitative analysis are usually all of the same normality, i.e., containing equivalent amounts of dissolved substances in equal volumes. In conducting the tests, approximately equal volumes of these solutions are mixed, as equal volumes contain the amounts of dissolved substances which satisfy the reaction equations. For example, binormal (2 *N*) solutions, containing 2 g-eq of dissolved substance per litre, are very often used.

It will be remembered that *a gram-equivalent of a substance is the amount chemically equivalent to 1 g (more precisely, 1.008 g) of hydrogen in a given reaction.* Thus, the gram-equivalent of HCl is equal to a gram-molecule (mole) or 36.5 g of it, as this is the amount of HCl containing 1 g of hydrogen; the gram-equivalent of H_2SO_4 is 1/2 mole (98/2 = 49 g); and of H_3PO_4, 1/3 mole (32.67 g).

The gram-equivalent of a base or salt is the weight containing the number of grams of the given metal required to replace 1 g of acidic hydrogen. Therefore the gram-equivalents of the substances listed below are:

KOH, NaOH, NaCl, KNO_3	1 mole
$Ca(OH)_2$, $Ba(OH)_2$, Na_2SO_4, $CuSO_4$	1/2 mole
$Al(OH)_3$, $FeCl_3$, $AlPO_4$, Na_3PO_4	1/3 mole
$Al_2(SO_4)_3$, $Ca_3(PO_4)_2$	1/6 mole

These examples show that *to find the gram-equivalent we must divide the gram-molecular weight by the basicity in the case of an acid, by the valency of the metal (or the number of* OH *groups) in the case of a base, and by the number of metal ions multiplied by the valency of the metal in the case of a salt.*

It must be pointed out, however, that we can apply these rules only if we take into account the particular reaction involved, as *in different reactions the same substance may have different gram-equivalents.* For example, it was stated above that the gram-equivalent of H_3PO_4 is 1/3 of a mole; but this is true only if all the three hydrogen ions of phosphoric acid are replaced by metal ions in the reaction.

In the reaction

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$$

phosphoric acid acts as a dibasic acid, and in the reaction

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$$

it acts as a monobasic acid. Therefore the gram-equivalent of H_3PO_4 is half of a gram-molecule in the first of these reactions, and is equal to a whole gram-molecule in the second.

It should also be borne in mind that the gram-equivalent of an oxidizing or reducing agent is calculated in a different manner.

If the two reacting solutions have different normalities, the volume of the solution of the higher normality should be decreased in proportion. Thus, *the solution volumes consumed in a reaction are inversely proportional to their normalities.* Denoting the volumes and normalities of the two solutions by v_1, N_1 and v_2, N_2 respectively, we can write:

$$\frac{v_1}{v_2}=\frac{N_2}{N_1} \text{ or } v_1 \cdot N_1 = v_2 \cdot N_2$$

In other words, *the products of the volume and the normality are equal for both solutions.*

With the aid of these rules it is easy to calculate the volume of reagent required for a particular reaction. For example, if we want to calculate the volume of 0.1 N $AgNO_3$ solution required for the reaction with 2 ml of 0.5 N $CaCl_2$ solution, we can write

$$x \cdot 0.1 = 2 \cdot 0.5$$

and hence

$$x=\frac{2 \cdot 0.5}{0.1}=10 \text{ ml}$$

It is clear from all this that the use of solutions of definite normality is very convenient in analytical reactions. Let us consider two concrete examples of the preparation of such solutions.

Example 1. To prepare 250 ml of 2 N barium chloride solution.

Solution. The salt crystallizes with two molecules of water, i.e., the formula is $BaCl_2 \cdot 2H_2O$. Therefore its molecular weight is 244.3. According to the foregoing, the gram-equivalent of $BaCl_2 \cdot 2H_2O$ is half a gram-molecule, or 244.3/2 = 122.2 g. Therefore 1 litre of 2 N barium chloride solution contains 244.3 g of the salt, and to prepare 250 ml (i.e., 0.25 litre) of 2 N solution we require $244.3 \times 0.25 = 61.1$ g $BaCl_2 \cdot 2H_2O$.

Weigh out this amount of the salt and dissolve it in a small amount of hot water. Cool the solution and dilute it in a measuring cylinder (or in a special "measuring flask" with a long narrow neck bearing a mark) to 250 ml.

Example 2. To prepare 1 litre of approximately 2 N hydrochloric acid solution from the concentrated acid of sp. gr. 1.19.

Solution. The gram-equivalent of HCl is equal to a gram-molecule or 36.5 g; therefore we must take $36.5 \times 2 = 73$ g HCl. Let us calculate the amount of concentrated hydrochloric acid containing this weight of hydrogen chloride. Chemical reference books contain tables of specific gravities of the most important acids and alkalies, showing the percentage contents corresponding to various specific gravities. From such a table we find that a solution of hydrochloric acid of sp. gr. 1.19 contains 37.23% HCl. Then, by proportion:

100 g of concentrated acid contains 37.23 g HCl

x g of concentrated acid contains 73 g HCl

Hence

$$x = \frac{73 \times 100}{37.23} = 196.1 \text{ g of the concentrated acid}$$

Instead of weighing out this amount of acid, it is more convenient to convert the weight to the volume. Since, by definition, each millilitre of the concentrated hydrochloric acid weighs 1.19 g, the required volume is

$$v = \frac{196.1}{1.19} = 165 \text{ ml}$$

Measure out (in a 200-ml measuring cylinder) the calculated volume of hydrochloric acid, dilute it to 1 litre in a one-litre measuring cylinder (or measuring flask), and mix the solution thoroughly.

In discussions of the theory of analysis it is usually more convenient to use molar rather than normal solution concentrations. The molar concentration, denoted by *M*, represents the number of gram-molecules of the substance dissolved in a litre of solution.

For example, a 0.1 *M* solution of sulphuric acid contains 0.1 of a gram-molecule or 9.8 g of H_2SO_4 per litre.

The concentration of any ion can also be stated in terms of molarity; this is the number of gram-ions per litre of solution. For example, if the concentration of acetate ions, CH_3COO^-, is 0.2 *M*, this means that 1 litre of solution contains $0.2 \times 59 = 11.8$ g of acetate ions.

5. Reaction Conditions. Sensitivity and Specificity of Reactions

A given analytical reaction must be conducted under *definite conditions which depend on the properties of the products formed; otherwise the result is unreliable.*

For example, precipitates which are soluble in acids obviously cannot form if the solution contains an excess of free acid. Similarly, precipitates soluble in alkalies do not form in alkaline solution. If a particular precipitate is soluble in both acids and alkalies it can be obtained only in a neutral solution, etc.

It is clear from these examples that *one of the most important conditions for a reaction is a suitable medium*, which may be adjusted as required by addition of acid or alkali to the solution.

Another important condition is the *temperature* of the solution. If the solubility of a precipitate rises sharply with the temperature it should not be prepared in a hot solution, and the reaction should be carried out in the cold, i.e., at room temperature, or sometimes the solution must even be cooled artificially. However, certain reactions proceed only on heating.

A very important condition is a *high enough concentration* of the particular ion in solution; at very low concentrations the reactions

fail. The cause is easy to see: any substance can be precipitated only when it is formed in solution at a concentration in excess of its solubility under the given conditions. If the solubility of the substance is very low, it is precipitated even at a very low concentration of the ion to be detected; the reaction is said to be *sensitive*. Conversely, if the solubility of the compound formed is considerable, the sensitivity of the reaction is low and the test succeeds only if the concentration of the ion to be detected is relatively high.

It is evident that we can apply similar reasoning to the sensitivity of reactions of other types, not only of precipitation reactions. For example, the flame test for volatile sodium salts is highly sensitive, as the flame is coloured by extremely small amounts of such salts.

The sensitivity of a reaction is characterized by two interconnected quantities—the detectable minimum and the dilution limit. The *detectable minimum* is the least amount of a substance or ion which can be detected by a given reaction under specified conditions. As this amount is very small, it is usually expressed in *micrograms*, i.e., millionths of a gram, denoted* by the symbol μg; 1 μg = $= 0.000001$ g $= 10^{-6}$ g.

The detectable minimum does not fully characterize the sensitivity of a reaction, because not only the absolute amount but also the concentration of the substance or ion detected is significant. Therefore the *dilution limit* is generally also stated; this is the lowest concentration of the substance (or ion) at which it can be detected by the given reaction. The dilution limit is represented by the ratio $1 : G$, where G is the weight of solvent per 1 part by weight of the substance or ion to be detected.

To determine the sensitivity of a reaction experimentally, it is performed repeatedly with solutions of progressively decreasing and accurately known concentrations of the test substance. These experiments are continued until the reaction no longer works; it is thus possible to determine the lowest concentration at which the reaction is still reliable.**

---

* The symbol γ (gamma) is sometimes used.

** If the concentration of the ion to be detected is considerably higher than the dilution limit, the result of the reaction (for example, precipitation) appears very rapidly. The reaction rate gradually falls with decreasing concentration of the ion, and at concentrations close to the dilution limit the reaction may give either positive or negative results. This is the "unreliable reaction region". As the concentration of the ion is decreased further the number of cases when the reaction is negative increases, and finally the reaction fails entirely. The dilution limit is generally taken to be the concentration of the ion at which one half of the total number of tests gives positive results.

Example. To determine the sensitivity of the reaction for the Ag^+ ion proceeding according to the equation

$$2AgNO_3 + K_2CrO_4 = \downarrow Ag_2CrO_4 + 2KNO_3$$

a solution of $AgNO_3$ containing 1 g Ag^+ (i.e., 1.57 g $AgNO_3$) per litre was prepared. It was found that the test is positive when this solution is diluted 25-fold, but on further dilution it becomes unreliable. Find the detectable minimum and the dilution limit for this reaction if it is carried out with a drop of solution 0.02 ml in volume.

Solution. Calculate the dilution limit:

$$\frac{1}{G} = \frac{\text{weight of } Ag^+}{\text{weight of water}} = 1 : 25{,}000$$

The detectable minimum is found by proportion:

25,000 ml of solution contains 1 g Ag^+

0.02 ml of solution contains m g Ag^+

hence:

$$m = \frac{0.02}{25{,}000} = 0.0000008 \text{ g} = 0.8\mu g$$

Therefore the detectable minimum m (expressed in micrograms, μg) and the dilution limit (G) are connected by the expression

$$m = \frac{V \cdot 10^6}{G}$$

where V is the volume of solution (in ml) taken for the reaction.

The reactions used for detecting the same ion may differ greatly in sensitivity; this is illustrated by the data in Table 1.

Table 1

Sensitivities * of Different Reactions for Cu^{++}

Reagent	Compound formed	Reaction effect	Detectable minimum, μg	Dilution limit 1 : G
HCl	$H[CuCl_3]$	Green solution	1	1 : 50,000
NH_3	$[Cu(NH_3)_4]Cl_2$	Blue solution	0.2	1 : 250,000
$K_4[Fe(CN)_6]$	$Cu_2[Fe(CN)_6]$	Brown precipitate	0.02	1 : 2,500,000

* The data in the table refer to tests carried out with drops of solution 0.05 ml in volume.

Table 1 shows that the reaction with $K_4[Fe(CN)_6]$ is the most sensitive; the amount of copper detectable in solution is 1/50 of

the amount detectable by the action of HCl and 1/10 of the amount detectable by NH_3.*

The sensitivity of a reaction may vary within wide limits in accordance with various factors. For example, it increases with increasing thickness of the solution layer used in the reaction, because weak turbidity or colour imperceptible in a thinner layer can be detected.

The reagent concentration is also of great importance; the sensitivity generally increases (up to a certain limit)** with the concentration. In many cases the sensitivity increases with the reaction time, especially if non-electrolytes or weak electrolytes are involved. Moreover, as already pointed out, a suitable medium and temperature are very important conditions which also have a strong influence on sensitivity.

The sensitivity of precipitation reactions can often be raised by addition of ethyl alcohol, which lowers the solubility of inorganic compounds, to the solution. The sensitivity may also be raised when the aqueous reaction mixture is shaken with some organic liquid which is immiscible with water (benzene, carbon tetrachloride, etc.). The precipitate collects at the boundary between the layers (it is "floated") and becomes easier to distinguish.

With highly sensitive reactions it is possible to detect very small amounts of various ions, so that it becomes unnecessary to use large amounts of the unknown substance or large volumes of solution.

It must be remembered, however, that the more sensitive the reaction the greater the danger of mistaking slight contaminations ("traces") of the reagents with the given ion for the presence of the ion in the unknown substance. To eliminate this danger, it is necessary to confirm the purity of the reagents by a *blank experiment* (i.e., an experiment with the reagents in the absence of the unknown substance).

It is also obvious that cleanliness of the apparatus and careful working in general are very essential for avoiding erroneous conclusions in analysis.

In addition to sensitivity, the *specificity* of a reaction is of very great significance in analysis.

A specific reaction for a given ion is one which can be used for detecting it, under experimental conditions, in mixtures with other ions. An example is the detection of the NH_4^+ ion by the action of alkali on heating; this is accompanied by evolution of ammonia,

---

* Only reactions with a detectable minimum not greater than 50 μg and a dilution limit not greater than 1:1,000 are normally used in qualitative analysis.

** This is discussed more fully in Sec. 26.

which is easily recognized by its odour and other properties:

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3 \uparrow$$

Of the compounds generally met in analysis, only ammonium salts give ammonia under these conditions. Therefore the alkali reaction is specific for the NH_4^+ ion.

However, specific reactions are not very numerous. Reactions giving the same or similar effects with several and sometimes with many ions are more common in analytical chemistry. Reactions which give a similar effect with only a limited number of ions are known as *selective*. The fewer the number of ions giving a positive test, the more selective is a given reaction.

It is often found that certain extraneous ions which do not react with a given reagent nevertheless influence the course of the reaction lowering the selectivity, altering the nature of the reaction products, etc. This influence increases with the concentration of the extraneous ion, and at a certain *limiting ratio* of the concentrations of the two ions the reaction can no longer be used. For example, the microcrystalloscopic reaction for Pb^{++} ions with KI, accompanied by the formation of characteristic PbI_2 crystals, is applicable only if the Cu^{++} concentration in the unknown solution is not more than 25 times the Pb^{++} concentration. Therefore in this case the limiting ratio is

$$Pb^{++} : Cu^{++} = 1 : 25$$

In some cases the interfering effects of extraneous ions may be prevented with the aid of *masking agents*, which are substances binding these ions into fairly stable complexes and thereby lowering their concentration in solution to a very great extent. For example, Cu^{++} ions, which give a black precipitate of CuS, interfere with the detection of Cd^{++} ions as a characteristic bright yellow CdS precipitate formed by the action of H_2S. If the test is performed in the presence of KCN, the Cu^{++} ion forms the complex ion $[Cu(CN)_4]^{---}$, which does not react with hydrogen sulphide. In this way the Cu^{++} ion is "masked" and does not interfere with detection of Cd^{++}. As in the absence of Cu^{++}, when H_2S is passed through the solution, a yellow precipitate of CdS is formed, indicating the presence of Cd^{++}.

6. Fractional and Systematic Analysis

With the aid of specific reactions it is possible to detect ions by the so-called *fractional method*, directly in separate portions of the unknown solution, without regard to other ions present; the order in which the separate ions are detected is immaterial.

If sufficiently reliable selective reactions are not available, and the selectivity cannot be raised in any way, the ions cannot be detected by the fractional method. In such cases it is necessary to work out a definite sequence for the detection of individual ions; this is *systematic analysis.* In this procedure each given ion is detected only after all the other ions which interfere with the detection (i.e., which also react with the reagent used) have been detected and removed from the solution.

As an illustration, let us consider the systematic analysis of a solution which may contain Ca^{++} and Ba^{++} ions. The most sensitive reaction for the Ca^{++} ion is formation of a precipitate of calcium oxalate, CaC_2O_4, by the action of soluble oxalates (salts of oxalic acid, $H_2C_2O_4$). For example:

$$CaCl_2 + (NH_4)_2C_2O_4 = \downarrow CaC_2O_4 + 2NH_4Cl$$

or, in ionic form

$$Ca^{++} + C_2O_4^{--} = \downarrow CaC_2O_4$$

This reaction is not specific for Ca^{++}, as Ba^{++} also gives a similar precipitate with this reagent. This means that we cannot start the analysis with detection of Ca^{++} but must first find whether Ba^{++} is present. The latter can be detected by the action of potassium chromate, K_2CrO_4, which gives a characteristic yellow precipitate of barium chromate:

$$Ba^{++} + CrO_4^{--} = \downarrow BaCrO_4$$

Since calcium chromate, $CaCrO_4$, is soluble in water, the presence of Ca^{++} does not interfere with the detection of Ba^{++}; therefore Ba^{++} can be detected in a separate portion of the unknown solution. If no $BaCrO_4$ precipitate is formed, Ba^{++} is absent and therefore Ca^{++} can be detected in another portion of the solution by the reaction with $(NH_4)_2C_2O_4$. On the other hand, if Ba^{++} is present it must be removed entirely from the solution before Ca^{++} can be detected. It is possible to remove Ba^{++} by the action of the same reagent, potassium chromate, enough being added to precipitate $BaCrO_4$ completely. To confirm that the precipitation is complete, a test is performed. The precipitate is filtered off and a small portion of the reagent is added to the filtrate. If no more precipitate forms, there is no Ba^{++} left in solution and Ca^{++} can be detected in it by the action of $(NH_4)_2C_2O_4$. In this case the formation of a white precipitate shows quite conclusively that Ca^{++} is present.

It is clear from this that in systematic analysis it is necessary to use *separation reactions* as well as *detection reactions* for individual ions.

Separation reactions are in most cases based on solubility differences between analogous compounds of the respective ions. For

example, the separation of Ba^{++} from Ca^{++} is based on the different solubilities of $BaCrO_4$ and $CaCrO_4$. Volatility differences may also be used in some instances. For example, NH_4^+ can be separated from K^+, Na^+ and Mg^{++} by evaporation of the solution followed by ignition of the dry residue. Ammonium salts are volatilized while the non-volatile potassium, sodium and magnesium salts remain in the basin used for the ignition.

Any separation achieves its aim only if it is sufficiently complete. This implies, in turn, that sufficient amounts of the appropriate reagents are used and that the precipitation conditions are suitable, or the ignition temperature and time are adequate, etc. A special experiment must always be performed to check that the separation is complete, otherwise the analytical results may be erroneous. The techniques for testing for complete separation will be described later.

7. Classification of Cations in Qualitative Analysis. Group Reagents

In systematic analysis of complex mixtures the ions are separated not singly but in whole groups; use is made of the same behaviour of ions in the same group with certain *group reagents*. For example, Ag^+, Hg_2^{++} and Pb^{++} form the sparingly soluble chlorides AgCl, Hg_2Cl_2 and $PbCl_2$ with Cl^-. Chlorides of all other cations are readily soluble in water.* Therefore if dilute hydrochloric acid is added to the unknown solution, these three cations are precipitated and separated from all the others.

If hydrogen sulphide gas is then passed into the acid solution after this separation, all cations giving sulphides insoluble in dilute acids are precipitated. These are the ions of bivalent mercury, copper, cadmium, bismuth, tin, antimony, and arsenic.

After the precipitated sulphides have been separated from the solution, the next group reagent, ammonium sulphide, $(NH_4)_2S$, is used for separating the next group of cations from the solution.

In contrast to the above examples of group separation of cations by precipitation as insoluble compounds, in some cases the group reagents dissolve particular components of the precipitate while others remain undissolved. For example, a group of ions (tin, arsenic, antimony, and bivalent mercury), the sulphides of which are soluble in Na_2S**, is separated in systematic analysis from the sulphides precipitated by the action of hydrogen sulphide on the acid-

* With the exception of certain basic chlorides such as BiOCl, SbOCl, etc. As these salts are soluble in acids, their formation may be prevented if the solution is made sufficiently acid.

** Owing to the formation of thiosalts such as Na_2SnS_3, Na_3AsS_3, etc.

ified solution; sodium sulphide is therefore the group reagent for this group.

The use of group reagents has considerable advantages, as the complex problem of analysis is subdivided into a number of simpler operations. If any group is entirely absent, its group reagent does not give any precipitate with the unknown solution. It is then pointless to carry out tests for the individual ions of this group, and a considerable amount of work, time and reagent can be saved. Thus, even if there are specific reactions for all the ions present, the systematic analytical procedure retains its significance, being more convenient and economic than fractional analysis of a substance of unknown composition. Conversely, if the composition of a substance is approximately known (as is often the case in practice) and it is necessary only to establish the presence or absence of one or two impurities, fractional reactions are more convenient.

Thus, *the classification of ions in analytical chemistry is based on different solubilities of their salts or hydroxides, allowing the separation of different groups of ions.* Leaving aside the classification of anions, which is to be considered in Chapter VIII, let us examine in more detail the classification of cations. These are subdivided into five groups in accordance with the different solubilities of their sulphides, chlorides, carbonates and hydroxides, as shown in Table 2.

On the basis of the data in Table 2, cations are separated into the analytical groups by the following procedure:

1. The unknown solution is acidified with dilute HCl. The ions of the first subgroup of Group IV are then precipitated* as the corresponding chlorides, AgCl, Hg_2Cl_2 and $PbCl_2$.

2. The precipitate is filtered off and gaseous H_2S is passed through the acid solution. Ions of the second subgroup of Group IV and ions of Group V are then precipitated as the sulphides—CuS, CdS, Bi_2S_3, (PbS), HgS, As_2S_3, Sb_2S_3, Sb_2S_5, SnS_2. To separate ions of Group V the precipitate is treated with Na_2S. This dissolves Group V ions (as the thiosalts of bivalent mercury, arsenic, antimony and stannic tin) while sulphides of Group IV cations remain in the precipitate.

3. After separation of the Group IV and V sulphides the solution is neutralized with NH_4OH and treated with $(NH_4)_2S$. This precipitates the sulphides (FeS, MnS, ZnS, CoS, NiS) and hydroxides [$Al(OH)_3$, $Cr(OH)_3$] of Group III cations.

4. Excess $(NH_4)_2S$ is decomposed by boiling with acetic acid and $(NH_4)_2CO_3$ is added to the solution. Group II cations are precipi-

---

* The Pb^{++} ion is precipitated incompletely by HCl. The part remaining in solution is subsequently precipitated by the action of H_2S.

tated as the carbonates ($BaCO_3$, $CaCO_3$ and $SrCO_3$) while Group I cations (K^+, Na^+ and Mg^{++}) remain in solution and are detected there*.

Table 2

Classification of Cations

Sulphides soluble in water		Sulphides insoluble in water (or water-insoluble hydroxides are formed instead)		
carbonates soluble in water *	carbonates insoluble in water	sulphides (or the hydroxides formed instead) soluble in dilute acids	sulphides insoluble in dilute acids	
Group I K^+, Na^+, NH_4^+, Mg^{++}, etc.	Group II Ba^{++}, Sr^{++}, Ca^{++}, etc.	Group III Al^{+++}, Cr^{+++}, Fe^{+++}, Fe^{++}, Mn^{++}, Zn^{++}, Co^{++}, Ni^{++}, etc.	Group IV (a) Subgroup 1—chlorides insoluble in water Ag^+, Pb^{++}, Hg_2^{++} (b) Subgroup 2—chlorides soluble in water Cu^{++}, Cd^{++}, Bi^{+++}	Group V Sulphides soluble in Na_2S Hg^{++}, As^{V}, As^{III}, Sb^{V}, Sb^{III}, Sn^{IV}, etc.**
No group reagent	Group reagent $(NH_4)_2CO_3$	Group reagent $(NH_4)_2S$	Group reagent H_2S in presence of HCl. The reagent precipitating Subgroup 1 is HCl	Group reagent Na_2S

* Magnesium carbonate dissolves only in the presence of ammonium salts.

** The symbols As^{V}, As^{III}, etc., indicate the valency of the element regardless of the ionic form in which the element is present in solution.

The cation classification adopted in this book generally agrees with the classification proposed by N. A. Menshutkin in 1871, and is the one most commonly used in the USSR.

* The NH_4^+ ion, which is introduced into the solution with the reagents during analysis, is detected previously in a separate portion of the unknown solution. The scheme given does not provide for the presence of Sn^{++} in the unknown solution; this must be oxidized to Sn^{++++} by means of H_2O_2 before treatment with H_2S.

A different numbering of the groups is sometimes used, where Group I consists of the cations precipitated by HCl, Group II contains those precipitated by H_2S, Group III those precipitated by $(NH_4)_2S$, Group IV those precipitated by $(NH_4)_2CO_3$, and Group V includes the cations K^+, Na^+, NH_4^+, and Mg^{++}, which have no group reagent. This numbering of the groups corresponds to the sequence in which the groups are separated in systematic analysis. However, Menshutkin's numbering, and therefore the order in which the groups are studied in a course of qualitative analysis, has a number of advantages: (1) it is consistent with the fundamental teaching principle of passing from the simpler to the more complex (from detection of alkali and alkaline-earth metal cations to detection of heavy-metal cations), which makes the study easier; (2) it allows the best coordination between the theoretical study of qualitative analysis and practical work; (3) it is in better agreement with the numbering of the groups in Mendeleyev's periodic system.

Although the basis of the analytical classification of ions is purely practical at first sight, it is by no means accidental. Indeed, the solubilities of the cation salts and hydroxides in question, forming the basis of the analytical classification, like all their other properties, must inevitably be functionally linked with the positions of the corresponding elements in the periodic system. The connection becomes quite evident if we examine the expanded form of the periodic system (Table 3). In this table the Roman numerals in the squares for each of the elements are the valencies of the cations, while the Arabic numbers give the structure of their electron shells (the numbers of electrons in the respective electron layers remaining after the atoms have lost their valency electrons).

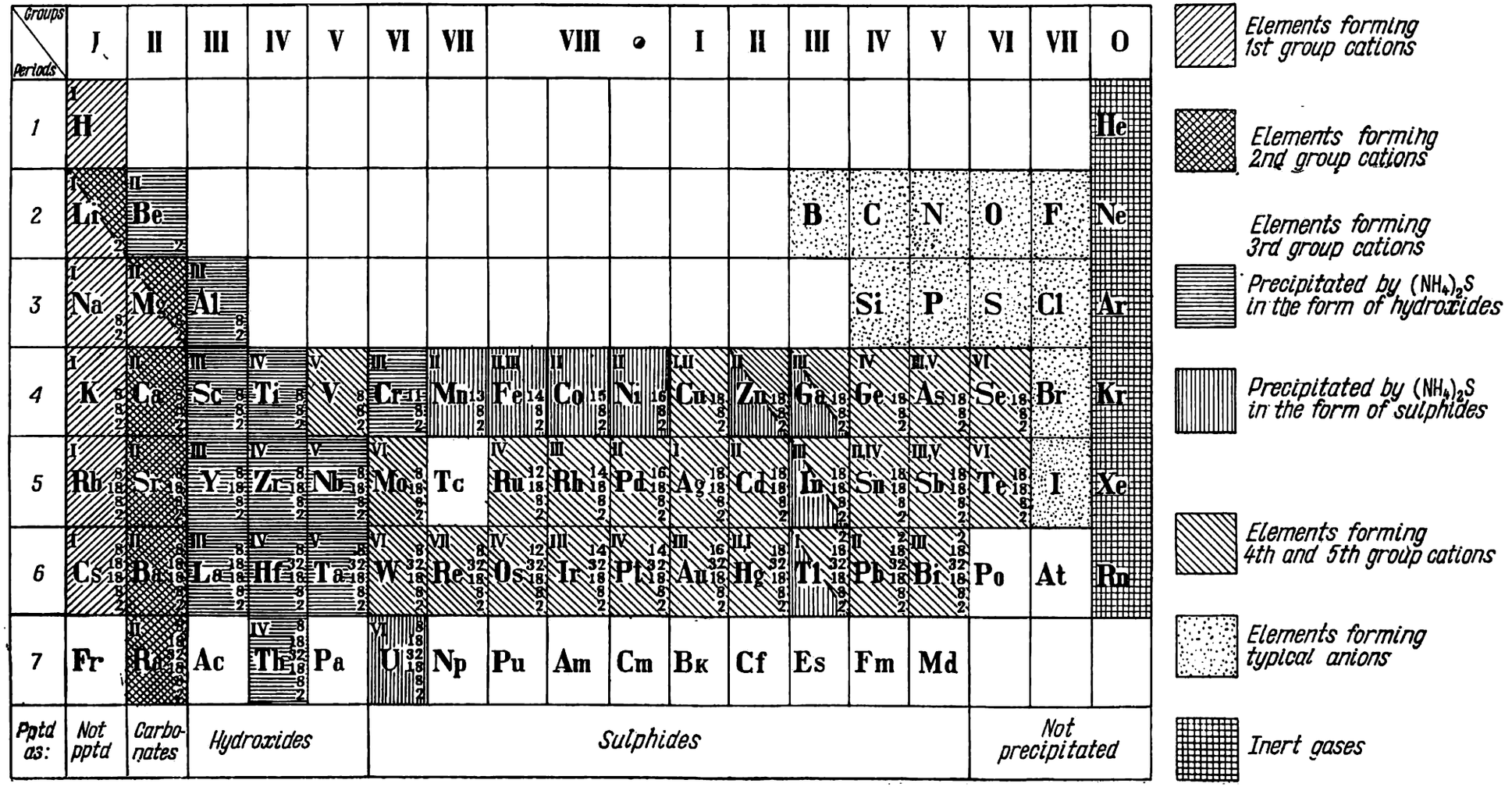
It is first clear from Table 3 that, with a few exceptions, the cations precipitated in the course of analysis as carbonates, hydroxides* and sulphides fit quite regularly into the periodic system. The cations forming sparingly soluble sulphides occupy the right-hand side of the table, starting with Group VI in the first half of the long periods and ending in the second half of the same group. Cations which do not form sparingly soluble sulphides are in Groups I-V in the left-hand side of the table. The cations of the first and second analytical groups are in the same groups of the periodic system. Cations of Group III, precipitated as hydroxides by ammonium sulphide, occupy Groups III-V of the periodic system in the left-hand side of the table. Finally, cations of Group III, precipitated as sulphides by $(NH_4)_2S$, are mainly in the middle of the fourth long period.

If we examine the electron shell structures of the cations we see that cations of analytical Groups I and II and those of the Group III

* Ammonium sulphide precipitates the hydroxides of the Group III cations which cannot exist as sulphides in the presence of water owing to hydrolysis.

Table 3

Analytical Groups of Cations and D. I. Mendeleyev's Periodic System of Elements


Groups
Periods
I
II
III
IV
V
VI
VII
VIII
I
II
III
IV
V
VI
VII
O
1 H He
2 Li Be B C N O F Ne
3 Na Mg Al Si P S Cl Ar
4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
5 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
6 Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
7 Fr Ra Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md
Pptd as:
Not pptd
Carbonates
Hydroxides
Sulphides
Not precipitated
Elements forming 1st group cations
Elements forming 2nd group cations
Elements forming 3rd group cations
Precipitated by $(NH_4)_2S$ in the form of hydroxides
Precipitated by $(NH_4)_2S$ in the form of sulphides
Elements forming 4th and 5th group cations
Elements forming typical anions
Inert gases

cations which are precipitated by $(NH_4)_2S$ as hydroxides have complete outer shells of two or eight electrons, like atoms of the inert gases. In contrast, cations of analytical Groups III, IV, and V, forming sparingly soluble sulphides, have either complete outer shells of 18 electrons, or incomplete shells transitional between 8-electron and 18-electron shells (in the middle of the long periods), or they have $18 + 2$ electrons in the two outer layers.

The cations having incomplete outer shells and 8 electrons in the next layer usually form sulphides soluble in acids (for example, in HCl), i.e., they belong to analytical Group III. Cations with incomplete outer shells and 18 electrons in the next layer form sulphides difficultly soluble in acids, i.e., they belong to analytical Groups V and IV.

Of course, there are some deviations from these relationships. However, this is clearly to be expected in view of the fact that certain cations are assigned arbitrarily to their particular analytical groups, the assignment often being determined by rather critical conditions of precipitation in group separation. For example, by its position in the periodic system the Mg^{++} cation should be included in cation Group II, and in fact, like $BaCO_3$, $SrCO_3$ and $CaCO_3$, magnesium carbonate is sparingly soluble in water; however, it dissolves in ammonium salts and therefore cannot be precipitated completely by $(NH_4)_2CO_3$. It is therefore preferable to separate Groups I and II in the presence of NH_4Cl so that the Mg^{++} ion remains in solution with Group I. That is why it is assigned to the latter group.

Consider another example. By its position in the periodic system, the Zn^{++} cation should be in analytical Group IV rather than III. Indeed, in contrast to all the other cations of Group III, it is precipitated by hydrogen sulphide from moderately acid solutions, like the cations of Groups IV and V. If the latter were precipitated at 0.01 *M* hydrogen ion concentration the Zn^{++} cation would be in Group IV and not III. However, as the precipitation is effected in strongly acid solution ($[H^+] \approx 0.3$ *M*) Zn^{++} remains in solution together with Group III. A number of other examples could be given.

It follows from this that some departures from regularity in the positions of the individual cations in the periodic system do not justify the conclusion that there is no correlation between that system and the analytical classification of cations. Of course, the nature and character of this correlation is not fully elucidated as yet, but its existence is undoubted. Formerly this correlation did not receive due attention; at present it is the subject of investigation by analysts.

8. Brief Historical Review of the Development of Analytical Chemistry

Practical techniques of analytical chemistry arose and developed far back in antiquity owing to the demands of the first chemical industries—ceramics and metallurgy. Initially, qualitative analysis consisted of identification of certain minerals and compounds by their properties. Quantitative analysis originated as the art of assaying, which was determination of the purity (fineness) of precious metals—gold and silver. The techniques were largely the same as those used in the production of these metals.

The development of analytical chemistry as a scientific discipline dates back to the middle of the 17th century, when Robert Boyle (1627-1691) introduced the concept of chemical elements as chemically indivisible components of complex substances, ultimately found in analysis. Boyle systematized all the previously known analytical reactions and proposed a number of new tests, and thus originated the principles of "wet-way" analysis. In particular, he was the first to use litmus and certain other vegetable colours as "indicators" for detection of acids and bases.

An important advance in the development of qualitative analysis was the separation of whole groups of metals (or rather, cations) from solution, introduced by T. O. Bergman (1735-1784) in the 18th century. This was the origin of systematic analysis which is used to the present day. Many other chemists, among whom special mention should be made of K. R. Fresenius (1818-1897), worked in the 19th century on further development and improvements of the procedure.

Another method of qualitative analysis, microcrystalloscopic analysis, originated in Russia in the 18th century owing to the work of M. V. Lomonosov (1711-1765) and especially of T. E. Lowitz (1757-1804). The researches of Russian scientists of the pre-revolutionary period on the utilization of crystal forms in analysis were brilliantly developed at the end of the 19th century by the classical work of the crystallographer E. S. Fedorov (1853-1919).

T. E. Lowitz, in addition to originating the microcrystalloscopic method of analysis, made a number of very important discoveries in the chemical field. The most significant is the discovery of adsorption phenomena, subsequently used extensively in the chromatographic method of analysis proposed by the Russian botanist M. S. Tsvett (1872-1919).

The founder of quantitative analysis as a scientific discipline is M. V. Lomonosov, who was the first to use systematic weighing of the original substances and of the products formed in chemical reactions. In 1756 Lomonosov experimentally confirmed the law

of conservation of matter, which he stated in general form in 1748. Lomonosov's law is the theoretical basis of quantitative analysis and is one of the most important laws of natural science.

On the basis of his experiments Lomonosov was the first to give the correct explanation of the part played by air in combustion and calcination* of metals and refuted Boyle's view that the increase in the weight of a metal when it is heated in air is due to addition of "fire matter" to the metal.

Subsequent development of the main techniques of gas analysis and the isolation of a number of important gases (H_2, O_2, N_2, Cl_2) led to rejection of the phlogiston theory. An especially important part in this respect was played by the work of the French chemist A. L. Lavoisier (1743-1794), who founded the "antiphlogiston chemistry" based on the oxygen theory of combustion. He was the first to determine the quantitative composition of air, water, and of a number of inorganic and organic substances.

V. M. Severgin (1765-1826) had a considerable influence on the development of analytical chemistry in Russia. In addition to analytical chemistry, he did a great deal of work on mineralogy and chemical technology, and is rightfully considered in the USSR to be its founder. He was the first in the world to write separate manuals on chemical analysis; before his time it was presented in the form of appendices to books on mineralogy, chemical technology, etc.

In 1796 Severgin published his book entitled *Manual on the Testing of Mineral Waters*, followed in 1800 by the first textbook of pharmaceutical chemistry. In 1801 he published his major work *The Assay Art, or Manual of Chemical Testing of Metallic Ores and Other Minerals*, in which all available material on analytical chemistry was creatively reviewed in the light of antiphlogiston chemistry and confirmed by a number of experiments. The book has a theoretical introduction on the scientific basis of analytical methods, and this distinguishes it favourably from well-known manuals published considerably later by foreign chemists, which were purely empirical in character.

Severgin enriched analytical chemistry by a number of new reactions and analytical techniques; in particular, he made extensive use of reactions taking place in the blow-pipe flame, mutual displacement of metals from salt solutions, and separation of metals (cations) by the action of alkalies, sodium carbonate, and similar reagents. He introduced into analytical practice a number of sensitive reactions for various ions, such as the reaction for Cu^{++} with ammonia, for Mn^{++} with saltpetre, etc.

---

* Conversion of a metal into a "calx" (oxide) when it is heated in air.

The use of the methods of quantitative analysis led to the discovery, at the beginning of the 19th century, of the stoichiometric laws (laws of constant composition, multiple proportions, and equivalents). The experimental confirmation of these laws due to the work of the English chemist J. Dalton (1766-1844) finally established the atomic theory in chemistry. Its introduction stimulated further development of quantitative analysis, as it became necessary to determine the atomic weights of the elements with the greatest possible accuracy. Much credit in this field is due to the famous Swedish chemist J. J. Berzelius (1779-1848), who determined very accurately (for that time) the atomic weights of 50 elements, devised many new methods for quantitative determination and improved earlier techniques. In particular, Berzelius devised a method for ultimate analysis of organic compounds, which was subsequently improved by J. Liebig (1803-1873) and other scientists. In 1824-1848 J. L. Gay-Lussac (1778-1850) introduced the volumetric method of quantitative analysis, which was extended further in the middle of the 19th century by the introduction of oxidation-reduction methods (permanganatometry and iodometry) and the use of indicators in precipitation methods.

In 1859 R. W. Bunsen (1811-1899) and G. R. Kirchhoff (1824-1887) developed the most important physical method of qualitative analysis—qualitative spectral analysis. Electrogravimetric analysis was also developed in the 19th century; it was originated by V. V. Petrov (1761-1834), who first effected the electrolysis of a number of chemical compounds (1803).

The first edition of the classical manual on qualitative and quantitative analysis, *Analytical Chemistry* by N. A. Menshutkin (1842-1907), an eminent chemist and teacher, was published in 1871. Menshutkin introduced the classification of cations by analytical groups, which has been adopted in this book.

The development of analytical chemistry during the second half of the 19th and in the 20th century is associated with advances in related branches of chemical science—inorganic, organic, and physical chemistry. First, we must mention the periodic law discovered by D. I. Mendeleyev (1834-1907) and his periodic system of the elements (1869), in which the elements are elegantly unified and a relationship is established between their properties and atomic weights. The periodic system was synthesis of everything valuable which had been created in chemistry during its existence as a science, and continues to serve as the basis for the understanding and further development of chemistry. The periodic system enabled analysts to utilize the analogy in the properties of elements for discovering new reactions and methods for determination of ions. For example, from the position of germanium, an element predicted by Mendeleyev,

in Group IV of the periodic system between silicon and tin it follows that the analytical reactions of germanium ions should resemble the reactions of silicon and tin ions of the same valency. In fact, like the Sn^{++++} ion, the Ge^{++++} ion is precipitated by hydrogen sulphide in acid solution as the sulphide GeS_2, which dissolves (like SnS_2) in NaOH, Na_2S, etc., to form thiosalts. Therefore the Ge^{++++} ion, like the Sn^{++++} ion, must be assigned to analytical Group V. On the other hand, it could be predicted that the GeO_3^{--} anion formed by quadrivalent germanium should resemble the SiO_3^{--} anion. In fact, both these anions react with ammonium molybdate $(NH_4)_2MoO_4$ to form the heteropoly acids $H_8[Ge(Mo_2O_7)_6]$ and $H_8[Si(Mo_2O_7)_6]$, which are similar in structure and chemical properties and which on reduction with the organic reagent benzidine form substances with an intense blue colour; this is used in analysis for detection of both these ions.

Numerous examples can be given of such analogies in chemical reactions, dependent on the positions of the respective elements in Mendeleyev's periodic system and used for discovery of new reactions.

For experimental verification of the periodic system it was necessary to determine with more accuracy the atomic weights of a number of elements, and this led to improvements in methods of quantitative analysis.

Nevertheless, the use of the periodic system in analytical chemistry still remained inadequate until recently. As was pointed out earlier, the analytical classification of ions was not correlated with the positions of the corresponding elements in the periodic system. Considerable attention has been devoted to this matter in recent years.

The rapid growth of organic synthesis had an enormous influence on the development of analytical chemistry. Some organic compounds proved to be very valuable reagents for various ions; analysis is greatly facilitated and accelerated by the use of such reagents. Wide potentialities for discovery of highly sensitive and specific reagents for various ions are offered to analytical chemistry by the large number of available organic compounds and by the possibility of altering their composition and structure by a great variety of methods, thereby influencing their properties as analytical reagents.

Organic reagents were first used in analytical chemistry by M. A. Il'insky (1856-1941) and L. A. Chugaev (1873-1922). Especially significant is the work of Chugaev, who proposed in 1905 a reaction for the Ni^{++} ion (p. 294) and raised the problem of studying the analytical properties of compounds known as internalcomplex salts. This problem is now among the most topical in analytical chemistry.

Organic reagents are used most widely in drop and colorimetric analysis. The drop method was developed in 1920 by N. A. Tananaev (1878-1959), who used it for fractional detection of ions. Important work on drop or spot analysis was also carried out by the Austrian chemist F. Feigl. The "chipless" method for analysis of metals and alloys was subsequently developed by Tananaev from the drop method. In this technique the metal or alloy is dissolved by surface application of a suitable solvent, such as HNO_3, and the resultant drop of salt solution is transferred to a strip of paper where the drop reaction is carried out. Tananaev also carried out a number of important investigations into the theory and practice of qualitative and quantitative analysis.

The rapid development of physical chemistry at the end of the 19th and the beginning of the 20th century also greatly assisted the progress of analytical chemistry. In the theory of analysis an especially important part was played by the introduction, by S. Arrhenius (1859-1927), of the theory of electrolytic dissociation (in 1887), which was used together with the law of mass action by W. Ostwald (in 1894) for providing a theoretical basis for a number of analytical reactions and experimental techniques, which previously were mainly empirical in character. The work of the German physical chemist W. Nernst (1864-1941), who formulated the solubility product rule and developed the theory of galvanic cells, and of L. V. Pisarzhevsky (1874-1938), who recognized oxidation-reduction reactions as processes involving electron transfer (1910-1914), was also important for analysis. Physical chemistry also enriched analytical chemistry by the theory of oxidation potentials, whereby it is possible to predict theoretically the direction of oxidation-reduction reactions, to calculate their equilibrium constants, to choose the most suitable oxidizing and reducing agents, and to solve a number of other most important problems.

The theory of A. N. Bakh (1857-1946) on the mechanism of oxidation-reduction reactions and the researches of N. A. Shilov (1872-1930) on conjugate oxidation-reduction reactions and adsorption phenomena are also of much importance for analytical chemistry. The advances made in the theory of oxidation-reduction processes made it possible to extend their field of application in volumetric analysis.

Apart from leading to valuable theoretical generalizations, the development of physical chemistry provided analysts with a number of new experimental methods and techniques. All these methods are of great significance and are widely used in research and industrial laboratories; this extends considerably the potentialities of qualitative and quantitative analysis and in many cases presents a number of valuable advantages over chemical methods. However,

the latter remain the basis for the development of physical and physico-chemical methods and therefore continue to play the leading part in analytical practice.

At the end of the 19th century an essentially new method of analysis was developed in Russia, mainly by N. S. Kurnakov (1860-1941) and his school. This method, known as physico-chemical analysis, consists of the determination of the chemical nature of complex systems (such as alloys, solutions and glasses) by study of the relationships between the composition and the physical properties of the systems rather than by isolation of the individual components. In physico-chemical analysis property-composition diagrams make it possible to find the most favourable conditions for chemical reactions, to establish the compositions of individual phases in heterogeneous systems, etc.

The demands of industry stimulated the growth of analytical chemistry even more than the progress of allied branches of science. The development of various industries induced rationalization of methods for chemical control of production, i. e., determination of the composition of the raw materials, intermediates, and finished products. These practical demands of industry were the most important for the origin and development of analytical chemistry as a science. These problems, essential for production, were solved by a number of scientific research organizations, institutes and factory laboratories. This resulted in unusually rapid growth of the amount of scientific research work in the field of analytical chemistry.

QUESTIONS AND PROBLEMS

1. What reactions are called sensitive? What are the characteristics of the sensitivity of a reaction?

2. To determine the sensitivity of the reaction for the Fe^{+++} ion with ammonium thiocyanate (NH_4CNS) a solution of an iron salt containing 1 g Fe^{+++} per litre was prepared and it was found that under certain conditions the test succeeds with the solution at 1,000-fold dilution, but becomes unreliable at higher dilutions. Find the dilution limit and the detectable minimum, taking into account that the red colour of the solution [due to the formation of ferric thiocyanate, $Fe(CNS)_3$] becomes noticeable when the reaction is performed with 2 ml of solution.

Answer. Dilution limit 1:1,000,000; detectable minimum 2 μg.

3. In microcrystalloscopic detection of the Ca^{++} ion as CaC_2O_4 the test is positive even with 0.001 ml of 0.001 *M* $CaCl_2$ solution. Calculate (a) the detectable minimum; (b) the dilution limit for this reaction.

Answer. (a) 0.04 μg Ca^{++}; (b) 1:25,000.

4. The dilution limit for the reaction for the K^+ ion with $NaHC_4H_4O_6$ (formation of $KHC_4H_4O_6$ precipitate) is 1:1,000. What is the lowest concentration (normality) of a KCl solution at which the K^+ ion can be detected by this reaction?

Answer. ~0.026 *N*.

5. Solutions of calcium salts give a white precipitate of $CaHPO_4$ with Na_2HPO_4. Given that this precipitate is soluble in acids (including acetic

acid) but is almost insoluble in hot water and alkalies, state whether this reaction can be carried out (a) on heating, (b) in the presence of acids, (c) in the presence of alkalies.

6. What reactions are called (a) specific; (b) selective? How can we detect ions for which there are specific reactions?

7. What is the essential principle of systematic analysis?

8. What are group reagents? What are the advantages of using group reagents in qualitative analysis?

9. What conclusions can be drawn about the composition of an unknown solution if it does not give precipitates with HCl, H_2S, $(NH_4)_2S$, or $(NH_4)_2CO_3$?

10. What arguments support the view that wet-way reactions used in qualitative analysis are ionic reactions? What are the advantages of the ionic nature of the reactions for analysis?

11. Why do all soluble calcium salts give a reaction with $(NH_4)_2C_2O_4$? Can this reagent be replaced by $Na_2C_2O_4$ for detection of Ca^{++}?

12. The action of silver nitrate ($AgNO_3$) on a solution of potassium chromate (K_2CrO_4) gives a characteristic dark red precipitate of Ag_2CrO_4. Will this reaction work if a solution of $Cr_2(SO_4)_3$ is used instead of K_2CrO_4? What is actually detected by the reaction when $AgNO_3$ is used as the reagent?

13. Write the following reaction equations in ionic form:

$$K_2CrO_4 + 2AgNO_3 = \downarrow Ag_2CrO_4 + 2KNO_3$$

$$Fe_2(SO_4)_3 + 3CaCl_2 = \downarrow 3CaSO_4 + 2FeCl_3$$

$$FeSO_4 + 2KOH = \downarrow Fe(OH)_2 + K_2SO_4$$

14. Name the substances which can be taken for the following reactions:

$$Pb^{++} + 2Cl^- = \downarrow PbCl_2$$

$$Ag^+ + Br^- = \downarrow AgBr$$

$$Cu^{++} + 2OH^- = \downarrow Cu(OH)_2$$

15. Solutions of $FeCl_3$, $Fe(NO_3)_3$ and $Fe_2(SO_4)_3$ give a red colour with ammonium thiocyanate owing to the formation of ferric thiocyanate, $Fe(CNS)_3$. Will this reaction work with $FeSO_4$ solution (free from ferric salts as impurities)?

16. What is the weight of $ZnSO_4 \cdot 7H_2O$ to be taken for preparation of 200 ml of 0.5 *N* solution?

Answer. 14.37 g.

17. What is the volume of 56% H_2SO_4, sp. gr. 1.46, to be taken for preparation of 5 litres of 2 *N* solution?

Answer. ~600 ml.

18. How many millilitres of 2 *N* Na_2CO_3 solution should be taken to prepare 250 ml of 0.35 *N* solution?

Answer. 43.75 ml.

CHAPTER II

CATIONS OF GROUP I

THEORETICAL ASPECTS

After the main concepts of qualitative analysis have been outlined in the preceding chapter we proceed to examine the reactions and course of analysis of cations in the individual groups. To understand this discussion it is necessary to know the basic principles of the theory of qualitative analysis.

Accordingly, the fundamental theoretical aspects are considered concurrently with a description of the reactions and course of analysis of cations of Groups I-IV. The most important of these are chemical equilibrium and the theory of solutions, which are discussed in this chapter.

9. The Law of Mass Action

Many of the reactions used in analytical chemistry are *reversible*, i. e., they proceed simultaneously in two opposite directions*. Examples are provided by the reactions used for detection and separation of Ba^{++} and Zn^{++} ions:

$$2BaCl_2 + K_2Cr_2O_7 + H_2O \rightleftarrows \downarrow 2BaCrO_4 + 2HCl + 2KCl$$

$$ZnCl_2 + H_2S \rightleftarrows \downarrow ZnS + 2HCl$$

In equations for reversible reactions the equality sign is replaced by the double arrow standing for reversibility ($\rightleftarrows$). Of a pair of simultaneously occurring reactions, the one proceeding from the left to the right of the equation ($\rightarrow$) is known as the *forward* reaction, and the one proceeding from right to left ($\leftarrow$) is the *reverse* reaction.

We know from the course of general chemistry that reversible reactions result in the establishment of *chemical equilibrium*, when the solution contains all the original substances and all those formed as the result of the reaction.

---

* It should be noted that the classification of reactions as reversible and irreversible is arbitrary. Strictly speaking, any reaction is more or less reversible, but in many cases the reversibility is so slight that it may be disregarded and the reaction may be regarded as practically irreversible.

Chemical equilibrium is attained because the rates of the forward and the reverse reactions become equal owing to changes in the concentrations of the reacting substances.

*The rates of chemical reactions are measured by the changes in the concentrations of the reacting substances per unit time**.

Any molecules or ions can react chemically only when they collide; the more frequent such collisions, the higher must the reaction rate be under given conditions. In the case of dissolved substances the frequency of collision between molecules or ions must obviously increase with their concentration.

For example, let us consider the reversible reaction

$$A+B \rightleftarrows C+D$$

where A, B, C and D are substances of different composition. The rate of the forward reaction is proportional to the concentrations of A and B. For convenience in calculation the concentrations of the reacting substances should be expressed on a molar basis (molar concentrations are expressed by the formulas enclosed in square brackets). We can therefore write:

$$v_1 = k_1 \cdot [A] \cdot [B] \qquad (1)$$

Here v_1 represents the rate of the forward reaction, and k_1 is the proportionality constant, known as the *reaction rate constant* or simply *rate constant.*

If the concentrations [A] and [B] are taken as 1 mole/litre, then

$$v_1 = k_1$$

Therefore the rate constant can be defined as the rate of a reaction if the concentration of each of the reacting substances is 1 *M* (or if the product of these concentrations is unity).

Similarly, for the rate of the reverse reaction (v_2) we can write**:

$$v_2 = k_2 \cdot [C] \cdot [D] \qquad (2)$$

If initially the substances A and B are taken for the reaction, their concentrations decrease as the reaction proceeds while the concentrations of C and D increase. Therefore the rate of the for-

---

* Since the reaction rate (v) is a variable quantity (like the rate of non-uniform motion), it can be expressed mathematically as the derivative of the concentration (c) with respect to time (t):

$$v = -\frac{dc}{dt}$$

The minus sign indicates that c decreases with increase of t.

** Since other substances are involved in this case, the value of the rate constant k_2 is different from the constant for the forward reaction.

ward reaction must gradually fall and that of the reverse reaction must increase from zero. It is evident that eventually the two rates must become equal.

The state of a system of reacting substances when the rates of the forward and reverse reactions are equal corresponds to chemical equilibrium.

When chemical equilibrium is attained, the numbers of molecules of A, B, C and D reacting per unit time are the same as the numbers formed as the result of the opposite reaction. Therefore at equilibrium the concentrations of all the reacting substances cease to change. It appears that the reaction has stopped. This is not in fact the case. Both reactions continue, but each counteracts the results of the other.

Since chemical equilibrium is not a state of rest, it is said to be a state of *mobile* or *dynamic* equilibrium.

Let us now consider at what relative concentrations of all four substances equilibrium is established between them. As we saw earlier, at equilibrium

$$v_1 = v_2$$

Substituting into this equation the values of v_1 and v_2 from Equations (1) and (2) we have

$$k_1 \cdot [A] \cdot [B] = k_2 \cdot [C] \cdot [D]$$

and we now take the concentrations to one side of the equation and the constants k_1 and k_2 to the other. This gives

$$\frac{[C] \cdot [D]}{[A] \cdot [B]} = \frac{k_1}{k_2}$$

But $\frac{k_1}{k_2}$, a ratio of two constants, must obviously be itself constant. Denoting it by K, we finally have

$$\frac{[C] \cdot [D]}{[A] \cdot [B]} = K$$

Similarly we find that equilibrium in the reaction

$$A + B + E \rightleftarrows C + D$$

becomes established when the concentrations of the substances satisfy the equation

$$\frac{[C] \cdot [D]}{[A] \cdot [B] \cdot [E]} = K \qquad (3)$$

If B and E are the same substance, the equations become

$$A + 2B \rightleftarrows C + D$$

and

$$\frac{[C]\cdot[D]}{[A]\cdot[B]^2}=K$$

Thus, in the general case, for the reaction

$$mA+nB \rightleftarrows pC+qD$$

(where m, n, p and q are the corresponding coefficients) the equilibrium condition is given by the equation

$$\frac{[C]^p\cdot[D]^q}{[A]^m\cdot[B]^n}=K$$

This equation is the mathematical expression of one of the most important laws of chemistry, *the law of mass action*, which may be stated as follows:

At equilibrium the product of the concentrations of the substances formed in a reaction divided by the product of the concentrations of the starting substances is a constant quantity for a given reaction at a given temperature, and is known as the equilibrium constant.

If the coefficient for a substance in the reaction equation is not unity, the concentration must be raised to the corresponding power.

The physical meaning of the equilibrium constant K is evident from the fact that it is equal to k_1/k_2, i.e., it shows how many times the rate of the forward reaction at a given temperature is greater than the rate of the reverse reaction at the same concentrations (equal to 1 mole/litre). If the equilibrium constant K is less than unity, this means that the reverse reaction proceeds at a higher rate. It follows that the direction of the reaction can be deduced from the numerical value of K. If the equilibrium constant K is very large, this means that the forward reaction goes almost to completion while the reverse reaction proceeds to a negligible extent. In other words, the equilibrium is shifted to the right. When K is very small, the reverse reaction predominates, and the equilibrium is strongly shifted to the left. Finally, if K is close to unity neither reaction predominates greatly over the other. In this case equilibrium becomes established at considerable concentrations of all four substances involved in the reaction, and the conversion of none is near complete.

The constancy of K implies that *it is independent of the initial concentrations of* A *and* B. Whatever these concentrations may be, the ratio $\frac{[C]^p\cdot[D]^q}{[A]^m\cdot[B]^n}$ at equilibrium always has the same value at constant temperature. On the other hand, any change of temperature leads to a change in the value of K. In other words, there is a definite value of the equilibrium constant for each temperature, just as any substance has a definite solubility at each temperature.

The law of mass action can be used for deliberate control of chemical equilibrium, which may be displaced in either direction. This is illustrated by the following example.

Suppose that at equilibrium in the reversible reaction

$$CO + H_2O \rightleftarrows H_2 + CO_2$$

we add (without altering the total volume of the gaseous mixture) one of the initial substances, such as H_2O vapour. The denominator of the fraction

$$\frac{[H_2]\cdot[CO_2]}{[CO]\cdot[H_2O]}$$

is then increased, and the fraction becomes less than K. Therefore to restore the equilibrium the denominator of the fraction must decrease while the numerator increases as the result of the forward reaction

$$CO + H_2O \longrightarrow H_2 + CO_2$$

the rate of which, as the result of the increase in the concentration of one of the reactants, exceeds the rate of the reverse reaction.

In the same way, addition of one of the reaction products, H_2 or CO_2 (increase of the numerator of the fraction) raises the rate of the reverse reaction. We therefore see that addition of one of the reacting substances causes a *shift of chemical equilibrium*, i.e., a change in the concentrations of all the substances involved in the reaction, which continues until the concentrations again satisfy the equation for the mass action law. *The reaction in which the added substance is expended is the one to undergo an increase in its rate.*

The following important conclusion is to be drawn from this: *to achieve the greatest possible conversion of one of the starting substances* (for example, CO) *we must introduce an excess of the reagent causing the conversion* (H_2O in the case under consideration). This is illustrated by the following example.

It is found experimentally that at 850°, with equal initial concentrations of CO and H_2O vapour, equilibrium becomes established when the concentrations of all the four substances are equal. For example, if 1 mole each of CO and H_2O are taken for the reaction, at equilibrium 0.5 mole of each remain and 0.5 mole each of H_2 and CO_2 are formed. The equilibrium constant at the given temperature is

$$K = \frac{0.5 \times 0.5}{0.5 \times 0.5} = 1$$

From this it is easy to calculate the equilibrium concentrations of each of the substances for any other initial concentrations of CO and H_2O. Let us perform this calculation for the case when 5 moles of H_2O is taken with 1 mole of CO (the total volume of the gaseous mixture being 1 litre).

Denote the number of moles of CO converted by x.

By the reaction equation, one molecule of H_2O reacts with each CO molecule and one molecule each of H_2 and CO_2 are formed; therefore the concentrations of these substances at equilibrium are:

$$[CO]=1-x \qquad [CO_2]=x$$
$$[H_2O]=5-x \qquad [H_2] =x$$

Substituting these values into the equilibrium equation, we have

$$\frac{x \cdot x}{(1-x)\cdot(5-x)}=1$$

and hence

$$x=\frac{5}{6}\approx 0.83 \text{ mole}$$

Thus, with a five-fold excess of H_2O 83% of the CO taken is converted, whereas with an equivalent amount of H_2O the conversion is only 50%.

10. Degree of Dissociation. Strong and Weak Electrolytes

It was stated earlier (Sec. 2) that wet-way reactions, the most commonly used in analytical chemistry, are ionic reactions. Since this is so, it is very important for the analyst to know the extent to which the compounds he uses are dissociated into ions.

We know that *the degree of electrolytic dissociation, denoted by* α, *is the fraction of a dissolved electrolyte which dissociates into ions.*

For example, the statement that "the degree of dissociation of acetic acid in 0.01 molar solution is 0.0419" means that at the stated concentration 4.19% of the total amount of acetic acid is present in a state of dissociation (in the form of ions) and 95.81% exists as undissociated molecules.

The degree of dissociation can be determined experimentally by a variety of methods, for example, from the electrical conductance of the solution, from the lowering of the freezing point of a solvent by a solute, etc.

By the theory of electrolytic dissociation, current flows through a solution by the movement of ions towards the oppositely charged electrodes. Accordingly, the higher the concentration and the higher the speed of the ions in solution, the more electricity is carried through the solution and the higher is its conductance.

It is found experimentally that with increasing dilution the *equivalent conductance* λ* of a solution gradually rises, approaching

* The conductance of a solution is the reciprocal of its resistance and is measured in reciprocal ohms. Thus, if the resistance of a solution is 100 ohms, its conductance is 0.01 reciprocal ohm. The equivalent conductance of a solution is the product of its specific conductance (the conductance of a column of solution 1 cm long and 1 cm^2 in cross section) and the volume of solution (in millilitres containing 1 gram-equivalent of the electrolyte.

a limiting value λ_∞. This limiting value, known as the *equivalent conductance at infinite dilution*, is reached in the case of strong (highly dissociated) electrolytes at concentrations of the order of 0.0001 *M* and does not alter on further dilution. This increase of λ may be due either to increase in the degree of dissociation when the solution is diluted, or to increased speed of the ions. In the classical electrolytic dissociation theory of Arrhenius it is assumed that the speed of the ions does not alter with changes in concentration. Therefore by this theory the increase of equivalent conductance with dilution is attributed exclusively to an increase of a quantity proportional to it, the degree of dissociation (α), which tends to the limiting value $\alpha = 1$ corresponding to complete dissociation. Hence we have

$$\frac{\alpha}{1} = \frac{\lambda}{\lambda_\infty}$$

and

$$\alpha = \frac{\lambda}{\lambda_\infty} \qquad (1)$$

After the equivalent conductance λ of a given solution has been measured experimentally, the degree of dissociation α of the dissolved electrolyte is calculated from Equation (1)*.

We know from the course in general chemistry that electrolytic dissociation in solution is not only the cause of conductance, but also causes deviations from van't Hoff's and Raoult's laws which relate to the osmotic pressure and depression of the freezing points or elevation of the boiling points of solvents containing dissolved electrolytes.

For example, if 1 mole of any non-electrolyte such as sugar, alcohol, glycerol, urea, etc., is dissolved in 1,000 g of water, the freezing point of the solvent is lowered to the same extent, by 1.86°, in each case. Since a mole of every substance contains the same number of molecules (6.03×10^{23}), the fact that substances of differing composition lower the freezing point of the solvent to the same extent indicates that the lowering depends only on the number of particles present in solution. Since the total number of particles is increased as the result of dissociation, it follows that electrolytes should cause abnormally large depressions of the freezing point. For example, if the degree of dissociation of a particular binary** electrolyte in a solution containing 1 mole in 1,000 g of water is 0.8 or 80%, the solution evidently contains 0.8 g-ion each of the anion and cation and 0.2 mole of undissociated molecules. The total number of particles present in solution therefore increases and corresponds to the number present in $2 \times 0.8 + 0.2 = 1.8$ moles and not in 1 mole. Therefore the freezing point depression should be also 1.8 times the depression produced by non-electrolytes, or approximately —3.35°. It is evidently easy to solve the converse problem, i.e., to find the degree of dissociation of a dissolved electrolyte from the experimentally determined freezing point of a solution of known

* The value of λ_∞ is found by calculation. It is the sum of the "ionic conductances" of the individual ions; these have been determined experimentally for numerous ions.

** If the molecule of an electrolyte forms only two ions on dissociation, the electrolyte is termed binary.

concentration. In addition to the depression of freezing point, other properties of solutions dependent only on the number of solute particles can be used for determination of α. These properties are the osmotic pressure, elevation of the boiling point, and lowering of the vapour pressure*.

Determinations of the degree of dissociation by different methods gave fairly close values; this led to the general acceptance of the Arrhenius theory.

The researches of the eminent chemists I. A. Kablukov and V. A. Kistyakovsky played an outstanding part in the development and acceptance of this theory.

However, later investigations showed that the classical theory of Arrhenius is satisfactorily applicable only to weak electrolytes, i.e., to substances which dissociate to a slight degree.

For strong electrolytes, the degree of dissociation of which is very high, it was necessary to propound a special theory, in which the influence of electrostatic attraction and repulsion forces between the ions on the speeds of the ions was taken into account.

The main points of the theory of strong electrolytes will be examined in Sec. 13. Here we merely note that, in accordance with that theory, all the methods mentioned above for determination of α give a correct idea of the actual degree of dissociation only for weak electrolytes, the ions of which are so far apart in solution that electrostatic forces have virtually no influence.

On the other hand, in the case of strong electrolytes which give rise to very numerous ions the influence of these forces cannot be ignored.

Therefore Equation (1), which is derived without regard for this influence, gives the *apparent* and not the true degrees of dissociation of strong electrolytes. The same applies to all other methods for determination of α**.

The degree of dissociation of electrolytes is of enormous importance in analysis, as the chemical activity of the respective substances depends on it. This is illustrated by the following facts. Conductance determinations on 1 *N* solutions of HCl and CH_3COOH show that hydrochloric acid is very highly dissociated, whereas the degree of dissociation of acetic acid is only 0.42%. If similar pieces of metallic zinc are added to each of these solutions, hydrogen is evolved rapidly in the HCl solution while in the CH_3COOH solution the liberation of hydrogen is extremely slow. When solutions of these acids act on $CaCO_3$ there is a similar difference between the rates of CO_2 evolution.

---

* Fuller details are given in textbooks of inorganic and physical chemistry.

** It will be shown in Sec. 13 that for a number of reasons the true degree of dissociation of any strong electrolyte is taken to be almost 100%.

The difference between the solvent powers of hydrochloric and acetic acids for substances sparingly soluble in water also indicates that these solutions differ in chemical activity. There are many substances (such as $BaCrO_4$, CaC_2O_4, ZnS) which are soluble in hydrochloric but not in acetic acid.

Thus, hydrochloric acid, which is dissociated to a considerable extent into ions, is a *strong* (chemically active) acid; the slightly dissociated acetic acid is a *weak* acid.

These facts are easily understood in the light of the theory of electrolytic dissociation. By the Arrhenius theory, the characteristic properties of acids are attributed to H^+ ions. The fact that H^+ ions are present in solutions of all acids is the reason why these solutions have a number of common properties, known as acidic properties. If this is so, the strength of an acid should increase with its content of H^+ ions, i.e., with its degree of dissociation.

Table II (see Appendix) gives experimental values for the degrees of dissociation of strong electrolytes; it is seen that the strong acids include HCl, HBr, HI, HNO_3 and H_2SO_4, which have very high apparent degrees of dissociation. In distinction from these, $H_2C_2O_4$, H_3PO_4, H_2SO_3 and HF are acids of moderate strength, while CH_3COOH, H_2CO_3, H_2S, HCN and other acids with low degrees of dissociation are weak acids.

Bases, like acids, have a number of properties in common; these are due to the presence of OH^- ions in their solutions. The strength of a base is determined by the concentration of OH^- ions formed in its solution, which depends on the degree of dissociation of the base. It is evident from the same Table II that KOH and NaOH are strong (chemically active) bases, while NH_4OH is an example of a weak base*.

Let us now consider the dissociation of di- and polybasic acids. Experiments show that they dissociate by stages. In the case of orthophosphoric acid (H_3PO_4), for example, first only one hydrogen ion is split off:

$$H_3PO_4 = H^+ + H_2PO_4^- \ (26\%)$$

The resultant $H_2PO_4^-$ anions partially dissociate to split off another H^+ ion:

$$H_2PO_4^- = H^+ + HPO_4^{--} \ (0.11\%)$$

Finally, the HPO_4^{--} ions split off the last hydrogen ion:

$$HPO_4^{--} = H^+ + PO_4^{---} \ (0.001\%)$$

The figures in brackets represent the percentage degrees of dissociation of the molecules or ions in 0.1 *M* H_3PO_4 solution. It is seen

* More modern concepts on the nature of acids and bases, which apply to non-aqueous as well as aqueous solutions, are presented in Sec. 31.

that the highest degree of dissociation corresponds to the first stage. The $H_2PO_4^-$ anion behaves as a weaker acid, while the HPO_4^{--} anion is a very weak acid. The reason is clear: it is more difficult for the positive H^+ ions to detach themselves from the negative $H_2PO_4^-$ ions than from neutral H_3PO_4 molecules, and even more difficult to detach themselves from the doubly charged HPO_4^{--} ions. Because of the stepwise dissociation, a solution of phosphoric acid has a fairly high content of $H_2PO_4^-$ anions, less HPO_4^{--}, and very little PO_4^{---} anions.

Other polybasic acids, and bases containing several hydroxyl groups in the molecule, dissociate similarly. In the case of bases OH^- ions are split off by stages, for example:

$$Ca(OH)_2 \rightleftarrows Ca(OH)^+ + OH^-$$

$$Ca(OH)^+ \rightleftarrows Ca^{++} + OH^-$$

While acids and bases show very great variations in the degrees of dissociation, nearly all soluble salts, with certain exceptions, are strong electrolytes, i.e., their apparent degrees of dissociation are high.

This applies even to salts formed from weak acids and weak bases. The high degree of dissociation of such salts may be illustrated by the following experiment. If a current of electricity is passed through solutions of acetic acid or ammonia of equal concentrations, an electric lamp included in the circuit gives a dull light. However, its light immediately becomes very bright if the two solutions are mixed and the electrodes are immersed in the mixture. The increased conductance of the solution is the result of increased concentration of ions in it owing to the formation of a highly dissociated salt:

$$CH_3COOH + NH_4OH = CH_3COONH_4 + H_2O$$

It follows from all this that *strong acids and bases and nearly all soluble salts are strong electrolytes. Weak acids and bases, water, salts such as* $Hg(CN)_2$, $HgCl_2$, *and certain other substances are weak electrolytes.*

11. Dissociation Constants of Weak Electrolytes

Let us examine the mechanism of dissociation of weak electrolytes with acetic acid as an example.

Dissociation is caused by the attraction exerted by neighbouring water molecules on the acetic acid molecules. It is known that the water molecule has an asymmetric structure as shown in Fig. 3. Therefore the "centres of gravity" of the negative and positive electric charges in the H_2O molecule do not coincide but lie at two different points in space. Such molecules are termed *dipoles.* Although a dipole is electrically neutral as a whole, it may exert electrostatic

forces on surrounding ions or dipoles. For example, they should turn with their negative poles towards positive ions (or positive poles of dipoles), and with their positive poles towards negative ones. This *orientation* of water dipoles gives rise to forces of electrostatic attraction, which tend to tear the electrolyte molecules apart into their constituent ions, and thereby greatly weaken the bonds between them. As a result, the energy of thermal motion of the molecules is sufficient to break the bonds, i.e., the molecules dissociate.

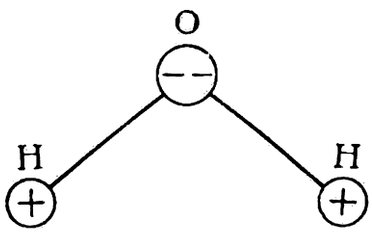


Fig. 3. Structure of the H_2O molecule

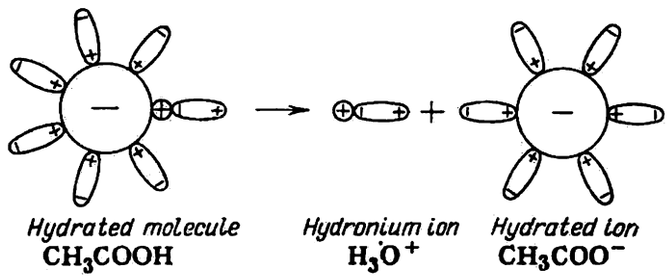


Fig. 4. Electrolytic dissociation of CH_3COOH molecules

Electrolytic dissociation is shown schematically in Figure 4. The ellipses represent water dipoles, the small circles with plus signs are H^+ ions, and the large circles with minus signs are CH_3COO^- ions. When these ions combine, undissociated molecules of acetic acid are formed.*

From this it follows that *dissociation results in the formation not of free ions but of compounds of ions with solvent molecules.* Such compounds have the general name of *solvates*; in particular, if the solvent is water they are known as ion *hydrates.* In a number of cases the formation of solvates or hydrates has been conclusively demonstrated by experiment. For example, it has been found that the free H^+ ion (i.e., proton) cannot exist in aqueous solutions but combines with a molecule of water to form a hydrate known as the *hydronium* ion:

$$H^+ + H_2O = H_3O^+$$

Figure 4 represents the formation of this ion by the dissociation of CH_3COOH in accordance with the equation

$$CH_3COOH + (n+1)\,H_2O \rightleftarrows H_3O^+ + [CH_3COO \cdot nH_2O]^-$$

* This interpretation of the dissociation of CH_3COOH, based on Kossel's theory, is somewhat simplified. It is more likely that H^+ and CH_3COO^- ions are not already present as such in the acetic acid molecules, but are formed as the result of attraction by water dipoles, which causes the conversion of the polar bond between H and O atoms in the CH_3COOH molecule into an ionic bond. The process then takes the course described in the text. Fuller details are to be found in textbooks of general chemistry.

The true cause of acidic properties is not the H^+ *ion as such but its hydrate, the hydronium ion* H_3O^+.

Nevertheless, for the sake of simplicity we shall continue to put the H^+ ion instead of the hydronium ion H_3O^+ in reaction equations. Similarly, we shall not indicate the presence of hydrate water in the formulas of all other ions, especially as the exact amount is unknown and may vary in accordance with the conditions.

Thus, the solution process cannot be regarded as purely physical. It involves chemical interaction between the solute and the solvent, leading to formation of hydrates or solvates. This idea was first put forward in 1887 by D. I. Mendeleyev, who took it as the basis for his *hydrate theory of solutions.*

Subsequently I. A. Kablukov suggested that ions are hydrated when electrolytes are dissolved. This hypothesis was confirmed experimentally. In this way the electrolytic dissociation theory of Arrhenius and the hydrate theory of Mendeleyev were unified.

The dissociation of the molecules of a weak electrolyte into ions is a reversible process; the resultant solvates of the oppositely charged ions are mutually attracted and may recombine to form solvated molecules when they collide as the result of their motion. With hydrate water disregarded, the dissociation of CH_3COOH may be represented by the following simplified equation:

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$

Like any other reversible process, dissociation leads to chemical equilibrium and obeys the law of mass action. We can therefore write:

$$\frac{[H^+]\cdot[CH_3COO^-]}{[CH_3COOH]} = K$$

or, in general form

$$\frac{c_c \cdot c_a}{c_m} = K \qquad (1)$$

Here c_c and c_a are the concentrations of the cation and anion, and c_m is the concentration of undissociated molecules of the electrolyte. The quantity K is the *dissociation constant* of the electrolyte. *It is a measure of the tendency of an electrolyte to split up into ions.* It is clear from the above equation that the greater the value of K the higher must be the ion concentrations c_c and c_a, i.e., the greater is the dissociation of the electrolyte.

We can easily obtain another form of the equation for the dissociation constant if we note that in the case of a binary electrolyte such as CH_3COOH the number of molecules dissociated into ions must be the same as the number of H^+ or CH_3COO^- ions formed. Therefore, if the acetic acid concentration is c moles/litre and its

degree of dissociation is α, the number of dissociated moles of CH_3COOH per litre of solution must be $c\alpha$ and

$$c_c = c_a = c\alpha$$

We can find the concentration of undissociated acetic acid molecules by subtracting the number of moles dissociated ($c\alpha$) from its total concentration (c). The result is

$$c_m = c - c\alpha = c(1-\alpha)$$

Substituting c_c, c_a and c_m into Equation (1), we have

$$\frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = K$$

or

$$\frac{c\alpha^2}{1-\alpha} = K \tag{2}$$

The equation written in this form is known as the *dilution law*. It represents the relationship between the degree of dissociation and the concentration of a weak electrolyte. If the electrolyte is fairly weak and its solution is not too dilute, its degree of dissociation α is low and $(1 - \alpha)$ differs little from unity.

Therefore in this case we can write

$$c\alpha^2 \approx K$$

and

$$\alpha \approx \sqrt{\frac{K}{c}} \tag{3}$$

This expression shows that the degree of dissociation increases with the dilution, i.e., with decreasing c; this is found experimentally to be the case.

We can easily determine the dissociation constant of an electrolyte by determining experimentally its degree of dissociation α for a particular concentration c and substituting these values into Equation (2).

Table 4 gives the results of such determinations for acetic acid. It is seen that although the degree of dissociation of CH_3COOH increases with decreasing concentration, the dissociation constant remains the same within the limits of experimental error.

The fact that K is independent of the solution concentration is an essential consequence of the law of mass action. The data in the table provide satisfactory experimental confirmation of this law. At the same time they may be regarded as experimental proof of the Arrhenius theory concerning the existence of equilibrium between ions

and undissociated molecules in solutions of weak electrolytes, which determines their behaviour.

It must be pointed out that in solutions of di- and polybasic acids there are several equilibria, corresponding to the different

Table 4

Degree of Dissociation and Dissociation Constant of Acetic Acid Determined for Various Concentrations

Concentration c, mole/litre	Degree of dissociation $\alpha=\frac{\lambda}{\lambda_\infty}$	Dissociation constant $\frac{c\alpha^2}{1-\alpha}=K$
0.2	0.00954 (0.954%)	1.82×10^{-5}
0.1	0.0136 (1.36%)	1.86×10^{-5}
0.01	0.0419 (4.19%)	1.83×10^{-5}
0.005	0.0585 (5.85%)	1.82×10^{-5}

dissociation stages, each with its own constant. For example. hydrogen sulphide is an acid which dissociates in two stages

$$H_2S \rightleftarrows H^+ + HS^-$$

and

$$HS^- \rightleftarrows H^+ + S^{--}$$

and we accordingly have (for 25°)

$$K_1=\frac{[H^+]\cdot[HS^-]}{[H_2S]}=5.7\times10^{-8}$$

and

$$K_2=\frac{[H^+]\cdot[S^{--}]}{[HS^-]}=1.2\times10^{-15}$$

The dissociation constants of various weak electrolytes are given in Appendix III.

From known values of K it is easy to calculate the degrees of dissociation and ionic concentrations in solutions of weak electrolytes, as shown in the following examples.

Example 1. Calculate the degree of dissociation and the concentrations of NH_4^+ and OH^- ions in 0.1 *N* NH_4OH solution (at 25°).

Solution. In Appendix III we find that the dissociation constant of NH_4OH at the stated temperature is 1.79×10^{-5}. Since the gram-equivalent of NH_4OH

is equal to one mole, a 0.1 N solution of NH_4OH is also a 0.1 M solution. Substituting the given values of K and c into Equation (3), we have

$$\alpha \approx \sqrt{\frac{1.79 \times 10^{-5}}{0.1}} \approx \sqrt{1.79 \times 10^{-4}} \approx 1.34 \cdot 10^{-2} \approx 1.34\%$$

The concentrations of NH_4^+ and OH^- ions are $c_c = c_a = c\alpha$, i.e.,

$$[NH_4^+] = [OH^-] = 0.1 \times 1.34 \times 10^{-2} = 1.34 \times 10^{-3} \text{ g-ion/litre}$$

Example 2. Find the H^+ ion concentration in 0.1 M H_2S solution (at 25°).

Solution. The greater part of the H^+ ions occurs in solution as the result of dissociation of H_2S at the first stage:

$$H_2S \rightleftarrows H^+ + HS^-$$

Dissociation at the second stage is so slight that it may be neglected without appreciable error. We can therefore use the equation

$$\frac{[H^+] \cdot [HS^-]}{[H_2S]} = K_1 = 5.7 \times 10^{-8}$$

We could use this value of K_1, as in the preceding example, to calculate α and then $c\alpha$, which is equal to the H^+ concentration.

However, it is more convenient to calculate $c\alpha$ direct from the formula

$$c_c = c_a = c\alpha = c \cdot \sqrt{\frac{K}{c}} = \sqrt{K \cdot c} \qquad (4)$$

Substituting the values of K and c into this expression, we have

$$[H^+] = \sqrt{5.7 \times 10^{-8} \times 0.1} = \sqrt{57 \times 10^{-10}} = 7.55 \times 10^{-5} \text{ g-ion/litre}$$

12. Shift of Ionic Equilibria. The Common Ion Effect

We saw in the study of the law of mass action that chemical equilibrium may be shifted in either direction by a change in the concentration of one of the reacting substances. A similar shift of equilibrium is easily achieved in electrolytic dissociation.

For example, if we add any acetate to a solution of acetic acid, we introduce with the salt a large amount of CH_3COO^- ions; these are known as *common* ions (i.e., the same as one of the ions of the given electrolyte). The numerator of the fraction

$$\frac{[H^+] \cdot [CH_3COO^-]}{[CH_3COOH]}$$

is greatly increased and the fraction becomes greater than the dissociation constant ($K = 1.86 \times 10^{-5}$). To restore the disturbed equilibrium H^+ and CH_3COO^- ions combine to form undissociated CH_3COOH molecules. *Therefore we can say that the degree of dissociation of a weak electrolyte* (CH_3COOH *in this case*) *is greatly lowered by addition of a strong electrolyte containing a common ion* (for

example, CH_3COONa or CH_3COOK) *to its solutions.* The H^+ ion concentration in the acetic acid solution is greatly diminished and *acetic acid behaves as a much weaker acid in the presence of its salts.* For example, it was stated earlier that CH_3COOH reacts slowly with metallic zinc. If a little CH_3COONa or CH_3COOK is added to CH_3COOH solution, evolution of hydrogen stops almost entirely.

Similarly it is easy to lower the OH^- ion concentration in NH_4OH solution by addition of an ammonium salt, which yields far many more NH_4^+ ions than are present in the original solution.

We can easily confirm this by the following experiment. To a solution of NH_4OH add a drop of the indicator phenolphthalein, which turns crimson in the presence of alkalies (i.e., in the presence of OH^- ions). After mixing, leave a part of the coloured solution for comparison; to another portion add a small amount of a solid ammonium salt, such as NH_4Cl, and shake the liquid to dissolve the added salt. The colour becomes much paler, indicating a considerable decrease of OH^- ion concentration in the solution.

By means of the equation for the dissociation constant it is easy to calculate the change in the concentration of a particular ion (for example, OH^-) resulting from the addition to an electrolyte solution of a definite amount of another electrolyte with a common ion. This is illustrated by the following example.

Example. Calculate the proportion in which the OH^- ion concentration in 0.1 *N* NH_4OH solution is decreased by addition of solid NH_4Cl to 1 *M* concentration.

Solution. In an earlier calculation (Sec. 11, Example 1) it was found that the OH^- ion concentration in 0.1 *N* NH_4OH solution is 1.34×10^{-3} g-ion/litre; it now remains to find what it will be in a mixture of NH_4OH with NH_4Cl. Let the required OH^- concentration be x.

In the mixture the NH_4^+ ion concentration is the sum of two quantities: x g-ions/litre formed by dissociation of NH_4OH, and 1 g-ion/litre formed by dissociation of NH_4Cl (as it is a strong electrolyte, it can be assumed to dissociate completely, and each dissociating NH_4Cl molecule yields one NH_4^+ ion). Therefore

$$[NH_4^+] = (1 + x) \text{ g-ions/litre}$$

To find the concentration of undissociated NH_4OH molecules we subtract the number of moles dissociated in 1 litre (i.e., x) from the total concentration; therefore $[NH_4OH] = (0.1 - x)$ moles/litre.

Substituting these values into the equation for the dissociation constant of NH_4OH, we have

$$\frac{[NH_4^+] \cdot [OH^-]}{[NH_4OH]} = \frac{(1 + x) \cdot x}{0.1 - x} = 1.79 \times 10^{-5}$$

By rearranging this equation we could obtain a complete quadratic equation which can be solved in the usual way.

However, the problem can be simplified in view of the fact that x is very small in comparison with 1 and 0.1, and it can therefore be disregarded without

appreciable error*. We can therefore write $\frac{1 \times x}{0.1} = 1.79 \times 10^{-5}$ and $x = 1.79 \times 10^{-6}$ g-ion/litre.

Comparing this result with the above value of 1.34×10^{-3} we see that as the result of addition of NH_4Cl the OH^- ion concentration in the solution decreased by a factor of

$$\frac{1.34 \times 10^{-3}}{1.79 \times 10^{-6}} \approx 750^{**}$$

It is therefore not surprising that, as is found experimentally, on addition of NH_4Cl the alkaline action of NH_4OH is much weakened.

The very considerable lowering of the concentration of a particular ion in solution by addition of an electrolyte with a common ion is widely used in practice.

The dissociation equilibrium of a weak electrolyte may be displaced by a decrease as well as by an increase of the concentration of one of its ions. For example, if we add an acid to a solution of NH_4OH and thereby bind the OH^- ions formed by dissociation into undissociated H_2O molecules we greatly decrease the numerator of the fraction

$$\frac{[NH_4^+] \cdot [OH^-]}{[NH_4OH]}$$

and it becomes less than K. The dissociation of NH_4OH molecules is therefore intensified. As a result, OH^- ions reappear in solution and the numerator of the fraction increases again. The undissociated molecules thus act as a sort of reserve which makes up, by dissociation, the loss of ions in solution. This can be stated in general form: *if we remove one of the substances in chemical equilibrium from the sphere of the reaction, we intensify the process in which this substance is formed.*

It was shown in Sec. 2 that, since the reactions used in analytical chemistry involve ions, it is more convenient to represent them by ionic equations. For the reaction in question, the ionic equation is

$$NH_4OH + HCl = NH_4Cl + H_2O$$

Since NH_4OH and H_2O are weak electrolytes, they are present in solution mainly as undissociated molecules. Conversely, the strong

---

* Small quantities can be disregarded by comparison with much larger ones only if they are added or subtracted, but not if they are multiplied or divided.

** It will be shown in Sec. 14 that this calculation is not exact because of the presence of a strong electrolyte (NH_4Cl) in solution; this gives rise to considerable electrostatic forces between the ions, which were not taken into account in the calculation.

electrolytes HCl and NH_4Cl should be represented as ions. We therefore have

$$NH_4OH + H^+ + Cl^- = NH_4^+ + Cl^- + H_2O$$

and

$$NH_4OH + H^+ = NH_4^+ + H_2O$$

The resultant equation shows that the reaction leads to disappearance of undissociated NH_4OH molecules and to an increase of the amount of NH_4^+ ions in solution. Similarly, the reaction between CH_3COOH and NaOH may be represented by the equation

$$CH_3COOH + OH^- = CH_3COO^- + H_2O$$

From all the foregoing it follows that *when ionic equations are written, the formulas of all the strong electrolytes present in solution must be represented by ions; the formulas of weak electrolytes, of sparingly soluble substances which are precipitated and of substances evolved as gases must be written in molecular form; ions which remain unchanged are not included in the ionic equation.*

13. The State of Strong Electrolytes in Solution

Whereas the dissociation of weak electrolytes leads to chemical equilibrium and can be characterized by a definite constant, *experiment shows that the dissociation of strong electrolytes does not conform to the law of mass action.* This means that if we determine the values of α for various concentrations of a strong electrolyte and substitute them into the equation

$$\frac{c\alpha^2}{1-\alpha} = K$$

the resultant values of K are different for different concentrations, as is shown in Table 5, referring to KCl solutions (compare this table with Table 4 for CH_3COOH solutions).

Table 5

Dissociation of KCl at 18°

Concentration, moles/litre	Degree of dissociation, α	Dissociation constant, $\frac{c\alpha^2}{1-\alpha} = K$	Concentration, moles/litre	Degree of dissociation, α	Dissociation constant, $\frac{c\alpha^2}{1-\alpha} = K$
2	0.712	3.52	0.1	0.862	0.536
1	0.756	2.34	0.01	0.942	0.152
0.5	0.788	1.46			

Other strong electrolytes show similar variations of K with concentration. Therefore, in distinction from weak electrolytes, *strong electrolytes do not have dissociation constants.*

The fact that solutions of strong electrolytes do not obey the law of mass action conflicts sharply with the classical Arrhenius theory of electrolytic dissociation and for a long time could not be explained satisfactorily. It is now explained by the *theory of strong electrolytes*, introduced by P. Debye and E. Hückel in 1923. V. K. Semenchenko, A. I. Brodsky, V. A. Pleskov and others played an important part in the experimental verification and further development of this theory. Because of its mathematical complexity, we can only give a very general outline of the theory here.

According to this theory, *strong electrolytes, unlike weak electrolytes, are completely dissociated in solution.* This view is supported by the fact that in the solid state strong electrolytes usually have ionic and not molecular crystal lattices. For example, since KCl crystals consist of K^+ anl Cl^- ions and not of molecules, it is reasonable to assume that they dissolve to give K^+ and Cl^- ions and not KCl molecules. However, if this is so, why do determinations of electrical conductance, osmotic pressure, freezing point depression or boiling point elevation indicate that the dissociation of strong electrolytes is apparently incomplete? The theory provides the following answer to this question.

The degree of dissociation of an electrolyte is usually determined from the equivalent conductance of its solutions. However, the equivalent conductance depends not only on the degree of dissociation but also on the speed of the ions. Under equal conditions the quantity of electricity carried by a given amount of ions must be the greater, the higher the speed of the ions. In the Arrhenius theory of electrolytic dissociation the speed of the ions is assumed constant, independent of the solution concentration. Therefore the Arrhenius theory attributes the variation of the equivalent conductance λ with dilution exclusively to the increase of α, the degree of dissociation of the electrolyte (see Sec. 10).

However, it is difficult to accept that the speeds of the ions in a solution of a strong electrolyte are independent of the concentration. Dissociation of the strong electrolyte results in the formation of very numerous ions which (especially in the more concentrated solutions) are so close together that electrostatic attraction and repulsion forces must act between them. *The action of these forces decreases the speeds of the ions; the closer together the ions, i.e., the higher the concentration of the solution, the greater is this effect.*

Owing to the existence of the interionic forces, each ion must be surrounded by an *ionic atmosphere*, a spherical layer of ions having a charge opposite to that of the central ion. When no external electrostatic forces act on the solution and no diffusion, chemical reac-

tions, and similar processes occur in it, the ionic atmosphere is completely symmetrical and therefore the attraction forces acting on the central ion are mutually balanced. On the other hand, if electrodes connected to a source of current are immersed in the solution this symmetry is continuously disturbed, as the ion and its atmosphere move in opposite directions (Fig. 5). The ionic atmosphere left by each ion then tends to pull it back and thus retards its motion. All the ions are subjected to this electrostatic retardation along their entire paths to the respective electrodes. As each ion is "pulled" out of its ionic atmosphere it enters the sphere of attraction of other ions, i.e., it becomes surrounded by a new ionic atmosphere, and so on. It is also evident that the denser the ionic atmosphere, i.e., the greater the concentration (and also the charges) of the corresponding ions in solution, the greater must be the decrease in the mobility of the ions.

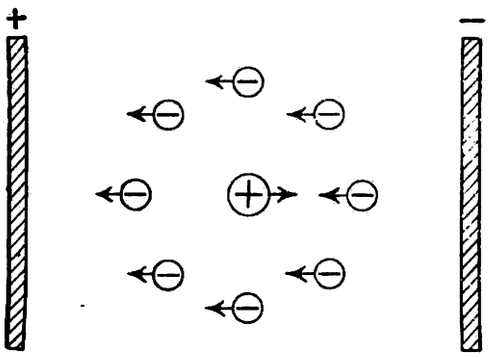


Fig. 5. Migration of an ion and the ionic atmosphere in electrolysis

Therefore in the case of strong electrolytes the increase of equivalent conductance with dilution depends not on the increased degree of dissociation of the electrolyte but on the increased speed of its ions owing to thinning of the ionic atmosphere and to the decrease of the interionic forces.

Thus, in solutions of strong electrolytes the ratio λ/λ_∞ can no longer be a measure of their true ionization (which is assumed to be 100%), but represents the influence of the interionic forces on the ability of the ions to carry electricity. Therefore the value of α calculated from the conductance of a solution of a strong electrolyte is not the true but the *apparent degree of dissociation.* In this case the value of α shows that because of the retarding action of the interionic forces the electrolyte carries the current as if not all the molecules were ionized (as is actually the case) but only a fraction α of them. The same applies to other methods for determining α, which again give not the true but the apparent degree of dissociation of strong electrolytes.

Later investigations have shown that the assumption of 100% dissociation of strong electrolytes is not quite accurate. Certain facts indicate that solutions of strong electrolytes also contain some undissociated molecules. However, their number is so small (very much less than was assumed by the Arrhenius theory) that their influence on the solution properties is negligible. Therefore in order to simplify the reasoning we shall assume that strong electrolytes are 100% dissociated.

14. Activity. Activity Coefficient

Interionic forces not only lower the conductance of solutions, but also influence the osmotic pressure, freezing point, boiling point, and the ability of the ions to take part in chemical action.

The term "activity" is used for assessment of this ability. *The activity (a) of an ion is its effective or apparent concentration in chemical reactions.* For example, if the activity of H^+ and Cl^- ions in 0.1 *M* HCl solution is 0.0814, this means that these ions act in chemical reactions as if their concentration is 0.0814 and not 0.1 g-ion/litre.* *The ratio of the activity to the true concentration of the ion, corresponding* (in the case of strong electrolytes) *to complete dissociation, is known as the activity coefficient (f).* In this case

$$f=\frac{0.0814}{0.1}=0.814$$

In general, representing activity by a and concentration of the ion by c, we have:

$$f=\frac{a}{c}$$

From this expression we have

$$a=f\cdot c$$

Thus, *the activity of an ion is the product of its concentration and the activity coefficient.*

As was already pointed out, the concentration c for strong electrolytes is calculated on the assumption of complete dissociation. In the theory of strong electrolytes the activity coefficient f is a measure of the influence of interionic forces on the ability of the ion to take part in chemical action. If $f<1$, the motion of the ion is hindered. In that case $a<c$, i.e., at that concentration (c g-ions/litre) the ions act as if their concentration is lower (a g-ions/litre). If $f=1$, then $a=c$. This means that the ion acts in accordance with its concentration in solution. In the case of strong electrolytes this occurs only in very dilute solutions (~ 0.0001 *M*), where the distances between the ions are so large that the interionic forces have practically no effect**. In the same way we can disregard interionic

---

* This is the mean value for the two ions, given by the expression $a=\sqrt{a_c\cdot a_a}$, where a_c and a_a are the activities of the cation and the anion.

** For reasons which cannot be considered here, the activity coefficients for concentrated solutions of strong electrolytes may be greater than unity. For example, in 1 *N* and 3 *N* HCl solutions the activity coefficients of the ions are 1.02 and 1.32 respectively.

forces in not very concentrated solutions of weak electrolytes, where only a very small proportion of the molecules is dissociated into ions. Therefore for such solutions we can also assume that $f = 1$ and $a = c$.

In accordance with the activity principle, the equation of the mass action law should contain ion activities and not their concentrations. Activity coefficients were originally introduced as certain empirical factors for extending the law of mass action to cases where it is inapplicable in its usual form. Their physical meaning was not clear. It was subsequently elucidated in the light of the theory of strong electrolytes, which made it possible to calculate f theoretically; the calculation is somewhat complicated, as the formula for calculating f contains three constants. For sufficiently dilute solutions (up to values of μ not greater than 0.1) it is relatively simple*:

$$\log f = -0{\cdot}5z^2 \frac{\sqrt{\mu}}{1+\sqrt{\mu}}$$

Here z is the ionic charge and μ is the "ionic strength" of the solution (see below).

For dilute solutions of strong electrolytes the theoretically calculated values are in satisfactory agreement with experimental data; this represents a great success for the theory.

It was noted earlier that for dilute solutions of weak electrolytes $f = 1$ and $a = c$. Therefore weak electrolytes obey the law of mass action fairly accurately. On the other hand, for strong electrolytes the activity of ions usually differs greatly from the concentrations, and therefore the law of mass action in its usual form is inapplicable to them. Neither can it be applied to weak electrolytes if extraneous strong electrolytes are present in solution**.

From all that has been said about the influence of interionic forces it follows that the activity coefficient depends not only on the concentration of the given electrolyte but also on the concentrations of all other electrolytes present in the solution. *The activity coefficient decreases with increase of the "ionic strength" of the solution, which depends on the concentrations and charges of all the ions present.*

---

* For values of μ up to 0.005, $1 + \sqrt{\mu}$ is very close to unity, and the formula is even simpler:

$$\log f = -0.5z^2\sqrt{\mu}$$

** For example, calculations of ion concentrations of a weak electrolyte in the presence of a strong electrolyte with a common ion, such as in the example in Sec. 12, cannot give accurate results if concentrations rather than activities are used. The procedure of more accurate calculation for an analogous case is examined at the end of this section.

The ionic strength μ of a solution is a measure of the intensity of the electrical field existing in the solution. It is calculated from the formula

$$\mu = {}^1/_2 (c_1 z_1^2 + c_2 z_2^2 + \ldots + c_n z_n^2)$$

where c_1, c_2, . . . c_n are the molar concentrations of the individual ions present and z_1, z_2, . . . z_n are their charges.

Thus, the ionic strength of a solution which is 0.1 *M* in respect to HCl and 0.2 *M* in respect to $CaCl_2$ is

$$\mu = {}^1/_2 (0.1 + 0.2 \times 2^2 + 0.5) = 0.7$$

Here 0.1 is the H^+ concentration, 0.2 is the Ca^{++} concentration, and 0.5 is the Cl^- concentration.

The value of the charge (valency) z is 1 for H^+ and Cl^-, and 2 for Ca^{++}.

Experiments show that in fairly dilute solutions of equal ionic strength the activity coefficients of ions having equal charge are approximately the same. The activity coefficients given in Table 6 may be used with sufficient accuracy for practical purposes.

Table 6

Activity Coefficients

Ionic strength, μ	Activity coefficients, *f*			
	univalent ions	bivalent ions	tervalent ions	quadrivalent ions
0.001	0.96	0.86	0.73	0.56
0.005	0.92	0.72	0.51	0.30
0.01	0.90	0.63	0.39	0.19
0.05	0.81	0.44	0.15	0.04
0.1	0.78	0.33	0.08	0.01

Since the solutions commonly met in analytical practice contain several different salts in high concentrations which are not accurately known, it is often impossible to use activity coefficients for various calculations. We will therefore confine ourselves to illustrating their use by one or two examples, and in all other cases we will replace activities by ion concentrations (calculated for strong electrolytes with the assumption that they are completely dissociated in solution). This simplification is quite permissible, because for the conditions used in qualitative analysis the usual purpose of calculations is merely to illustrate some theoretical aspect, and a high

degree of accuracy is not required. These simplified calculations usually give good qualitative agreement with experimental results. If no such agreement occurs, this will be pointed out at the time.

Example. To demonstrate calculations with the use of activity coefficients, let us calculate the activity of hydrogen ions (a_{H^+}) in a solution containing 0.1 mole CH_3COOH and 0.05 mole CH_3COONa per litre.

Owing to the presence of a strong electrolyte (CH_3COONa), the usual form of the equation for the dissociation constant of acetic acid

$$\frac{[H^+]\cdot[CH_3COO^-]}{[CH_3COOH]}=K$$

cannot give accurate results, as K varies with the ionic strength of the solution. To obtain accurate results, we must replace concentrations by activities

$$\frac{a_{H^+}\cdot a_{CH_3COO^-}}{a_{CH_3COOH}}=K_a \qquad (1)$$

where K_a is the *thermodynamic dissociation constant* of acetic acid, with the value of 1.75×10^{-5} (at 25°). In contrast to the ordinary (concentrational) dissociation constant (K), K_a remains constant in the presence of strong electrolytes.

Solving Eq. (1) for a_{H^+}, we have

$$a_{H^+}=K_a\cdot\frac{a_{CH_3COOH}}{a_{CH_3COO^-}}=K_a\frac{[CH_3COOH]\cdot f}{[CH_3COO^-]\cdot f_1}$$

The activity coefficient (f) of undissociated CH_3COOH molecules is taken as 1, and their concentration may be regarded as almost the same as the total concentration of acetic acid in solution, 0.1 M. Similarly, the concentration of CH_3COO^- anions may be taken as equal to the concentration of the salt (0.05 M), as free acetic acid gives rise to very few of these ions. To find the activity coefficient of these anions (f_1) we must calculate the ionic strength μ of the solution. In this calculation the small amounts of H^+ and CH_3COO^- ions formed by dissociation of free CH_3COOH may be neglected, and only the concentrations of the Na^+ and CH_3COO^- ions formed by dissociation of the salt need to be taken into account. As these concentrations are equal to the total concentration of the salt, 0.05 g-ion/litre, we have

$$\mu=\frac{1}{2}(0.05\times1^2+0.05\times1^2)=0.05$$

Table 6 shows that for this ionic strength the activity coefficient for univalent ions is 0.81. Therefore

$$a_{H^+}=1.75\times10^{-5}\times\frac{0.1}{0.05\times0.81}=4.6\times10^{-5}\text{ g-ion/litre}$$

Thus, in reactions involving hydrogen ions this solution acts as if the hydrogen ion concentration is 4.6×10^{-5} g-ion/litre. The true concentration is somewhat higher than this; it can easily be calculated from the equation

$$a_{H^+}=[H^+]\cdot f$$

Since the ionic strength of the solution is 0.05, the value of f, as for other univalent ions, is 0.81. Therefore we can write

$$4.6 \times 10^{-5} = [H^+] \times 0.81$$

and hence

$$[H^+] = \frac{4.6 \times 10^{-5}}{0.81} = 5.3 \times 10^{-5} \text{ g-ion/litre}$$

15. Dissociation of Water. The Hydrogen Ion Exponent (pH)

The reactions used in analytical chemistry take place in aqueous solutions in most cases. Water is a weak electrolyte which ionizes, although very slightly, as follows:

$$H_2O \rightleftarrows H^+ + OH^-$$

The fact that even the purest water, entirely free from dissolved electrolytes, has measurable although very low conductance shows that such dissociation occurs.

The degree of dissociation of water can be calculated from its conductance. It is found to be very low. For example, at room temperature (22°) only 1/10,000,000 mole or 1×10^{-7} mole of H_2O is dissociated per litre of water. Since each H_2O molecule gives an H^+ and an OH^- ion on dissociation, the concentrations of these ions in pure water are equal:

$$[H^+] = [OH^-] = 10^{-7} \text{ g-ion/litre (at 22°)}$$

As for other weak electrolytes, the ionization of H_2O molecules can be characterized by its dissociation constant*. This corresponds to the equation

$$\frac{[H^+] \cdot [OH^-]}{[H_2O]} = K = 1.8 \times 10^{-16}$$

This equation may be made more simple and convenient. For this we take $[H_2O]$ to the right-hand side:

$$[H^+] \cdot [OH^-] = K \cdot [H_2O]$$

---

* The numerical value of the dissociation constant of water can be calculated as follows. As already stated, the concentrations of H^+ and OH^- ions in water at 22° are both 1×10^{-7} g-ion/litre. At the stated temperature 1 litre of water weighs 997.8 g, and its molecular weight is 18.02; therefore 1 litre of water contains

$$[H_2O] = \frac{997.8}{18.02} = 55.37 \text{ moles } H_2O$$

Hence we have

$$K = \frac{[H^+] \cdot [OH^-]}{[H_2O]} = \frac{1 \times 10^{-7} \times 1 \times 10^{-7}}{55.37} = 1.8 \times 10^{-16}$$

Since water is present almost entirely in the form of undissociated H_2O molecules, any change in the degree of dissociation has very little effect on the concentration of the latter. Therefore $[H_2O]$ in the above equation may be regarded as practically constant. At the same time K is also constant. Therefore all the right-hand side of the equation, and hence the product $[H^+]\cdot[OH^-]$, must likewise be constant. This constant is known as the *ionic product of water*, represented by the symbol K_{H_2O}. Therefore

$$[H^+]\cdot[OH^-]=K_{H_2O}$$

At 22° in pure water $[H^+] = [OH^-] = 1 \times 10^{-7}$, and therefore at that temperature

$$K_{H_2O}=1\times10^{-7}\times1\times10^{-7}=1\times10^{-14}$$

Table 7 shows that K_{H_2O} increases rapidly with the temperature.

The equation $[H^+]\cdot[OH^-] = K_{H_2O}$ has the following meaning. *No matter how the concentrations of* H^+ *or* OH^- *ions may vary, their product in any aqueous solution is an (approximately) constant value,* 1×10^{-14}, *at room temperature* (22°)*.

Table 7

Ionic Product of Water (K_{H_2O}) at Various Temperatures

Temperature, °C	K_{H_2O}	$[H^+] = [OH^-]$	Temperature, °C	K_{H_2O}	$[H^+] = [OH^-]$
0	0.13×10^{-14}	0.36×10^{-7}	40	3.8×10^{-14}	1.95×10^{-7}
10	0.36×10^{-14}	0.59×10^{-7}	50	5.6×10^{-14}	2.4×10^{-7}
20	0.86×10^{-14}	0.93×10^{-7}	60	12.6×10^{-14}	3.5×10^{-7}
22	1.00×10^{-14}	1.00×10^{-7}	80	34×10^{-14}	5.8×10^{-7}
30	1.89×10^{-14}	1.37×10^{-7}	100	74×10^{-14}	8.6×10^{-7}

As already stated, in pure water

$$[H^+]=[OH^-]=1\times10^{-7} \text{ (at 22°)}$$

These are also the concentrations of these ions in any neutral solution.

---

* Strictly speaking, it is the product of the activities rather than the concentrations of the H^+ and OH^- ions which is constant. Since the dissociation of H_2O molecules is very slight, in pure water these activities are practically equal to the concentrations ($f = 1$). However, in the presence of extraneous electrolytes the $[H^+]$ and $[OH^-]$ concentrations differ appreciably from their activities. Nevertheless, for reasons already stated (Sec. 14), we will use the approximate value of the ionic product of water, calculated from the above equation, especially as this is quite adequate for our purposes.

If an acid is added to pure water and the H^+ ion concentration is thereby raised above 1×10^{-7}, the OH^- ion concentration is lowered to less than 1×10^{-7} in approximately the same proportion. Therefore in acid solution

$$[H^+] > 1 \times 10^{-7}; \quad [OH^-] < 1 \times 10^{-7} \quad \text{and} \quad [H^+] > [OH^-]$$

Similarly, in alkaline solution

$$[OH^-] > 1 \times 10^{-7}; \quad [H^+] < 1 \times 10^{-7} \quad \text{and} \quad [H^+] < [OH^-]$$

It follows that *any aqueous solution, whatever its reaction, must contain both* H^+ *and* OH^- *ions.* Since their concentrations are inversely proportional, as represented by the equation $[H^+] \cdot [OH^-] = K_{H_2O}$, the reaction (acidity or alkalinity) of any solution may be characterized quantitatively by its H^+ ion concentration. Instead of the H^+ ion concentration it is more convenient to use its negative logarithm, denoted by the symbol pH and termed the *hydrogen ion exponent.*

Therefore*

$$pH = -\log [H^+]$$

Hence we have, for example, at $[H^+] = 1 \times 10^{-4}$ g-ion/litre $pH = -(-4) = 4$; similarly, if $[H^+] = 5 \times 10^{-10}$ g-ion/litre, $pH = -\log 5 \times 10^{-10} = -(0.70-10) = 9.30$**.

It is obvious that the first solution (pH = 4) has an acid reaction, because $[H^+]$ in it is greater than 1×10^{-7} g-ion/litre. Conversely, the reaction of the second solution (pH = 9.30) is alkaline, as its $[H^+]$ is less than 1×10^{-7} g-ion/litre.

Therefore *in acid solutions* $pH < 7$, *in alkaline solutions* $pH > 7$, *and in neutral solutions* $pH = 7$. It is also easy to see that *the acidity of a solution increases with decrease of* pH *and the alkalinity increases with increase of* pH. For example, a solution is more acid at pH = 2 than at pH = 4, as the H^+ ion concentration in the former case (1×10^{-2} g-ion/litre) is 100 times as high as in the latter (1×10^{-4} g-ion/litre). Similarly we find that a solution is more alkaline at pH = 12 than at pH = 9. In the former case the OH^- ion concentration is

$$\frac{1 \times 10^{-14}}{[H^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-12}} = 1 \times 10^{-2} \text{ g-ion/litre,}$$

and in the second it is $\frac{1 \times 10^{-14}}{1 \times 10^{-9}} = 1 \times 10^{-5}$ g-ion/litre, which is less by a factor of 1,000.

---

* pH is defined more accurately as the negative logarithm of the H^+ ion activity, i.e., $pH = -\log a_{H^+}$.

** In pH calculations logarithms are always rounded off to within 0.01.

All the foregoing may be schematically represented as follows*:

pH	0 1 2 3 4 5 6	7	8 9 10 11 12 13 14
Reaction of solution	Acid ←	Neutral	→ Alkaline

The extreme pH values in this scheme roughly correspond to the hydrogen ion concentrations of 1 *N* HCl solution (pH $\approx$ 0) and 1 *N* NaOH solution (pH $\approx$ 14). Of course, more acidic solutions with pH <0 and more alkaline ones with pH >14 are possible. However, such cases are not usually of practical interest and are therefore not included in the scheme.

The hydroxyl ion exponent, like the hydrogen ion exponent, is sometimes used; it is denoted by the symbol pOH, such that

$$pOH = -\log [OH^-]$$

If the equation

$$[H^+] \cdot [OH^-] = 1 \times 10^{-14}$$

is expressed in logarithmic form and the signs of the logarithms are then reversed, we have

$$pH + pOH = 14 \text{ (at } 22°)$$

For solving various problems it is often necessary to convert $[H^+]$ to pH and vice versa. It is also sometimes necessary to calculate the pH of a solution of some acid or base, etc. Such calculations are illustrated by the following examples.

Example 1. The H^+ ion concentration in a solution is 5×10^{-4}. Calculate the pH and pOH of the solution.

Solution.

$$pH = -\log [H^+] = -\log 5 \times 10^{-4} = -(\log 5 + \log 10^{-4}) =$$
$$= -(0.70 - 4) = 3.30; \quad pOH = 14 - pH = 14 - 3.30 = 10.70$$

Example 2. Carry out a similar calculation for a solution in which $[H^+]$ is 4.5×10^{-11}.

Solution.

$$pH = -\log 4.5 \times 10^{-11} = -(0.65 - 11) = 10.35$$
$$pOH = 14 - 10.35 = 3.65$$

Example 3. Find the $[H^+]$ and $[OH^-]$ ion concentrations of a solution having pH = 4.87.

Solution.

$$\log [H^+] = -pH = -4.87 = 5.13, \text{ hence}$$
$$[H^+] = 1.35 \times 10^{-5}; \quad [OH^-] = \frac{10^{-14}}{1.35 \times 10^{-5}} = 7.41 \times 10^{-8}$$

* The horizontal arrows in the scheme indicate the directions in which the acidity and alkalinity of the solution increase.

Example 4. Find the pH of a 0.003 *N* HCl solution.

Solution. We know that HCl is dissociated almost completely. Since each molecule yields one hydrogen ion on dissociation, $[H^+] = 3 \times 10^{-3}$. Therefore

$$pH = -\log 3 \times 10^{-3} = -(0.48 - 3) = 2.52$$

Example 5. Find the pH of a 0.05 *N* NaOH solution.

Solution. $[OH^-] = 5 \times 10^{-2}$. Therefore

$$pOH = -\log 5 \times 10^{-2} = -(0.70 - 2) = 1.30$$

$$pH = 14 - 1.30 = 12.70$$

Example 6. Derive a formula for calculating the pH of a solution of a weak monobasic acid (HA) and use it to calculate the pH of 0.1 *M* formic acid (HCOOH) and hydrogen sulphide (H_2S).

Solution. The equation for the dissociation of the acid HA

$$HA \rightleftarrows H^+ + A^-$$

shows that equal amounts of H^+ and A^- ions are formed. Therefore their concentrations in solution are equal. If the acid solution is not too dilute, the acid is nearly all present in the form of undissociated molecules. Therefore we may assume that $[HA] = c_{acid}$. We then have

$$K_{acid} = \frac{[H^+] \cdot [A^-]}{[HA]} = \frac{[H^+]^2}{c_{acid}}$$

and hence

$$[H^+] = \sqrt{K_{acid} \cdot c_{acid}} \qquad (1)$$

To convert $[H^+]$ to pH, we take logarithms and reverse the signs. We then have

$$-\log [H^+] = -\frac{1}{2} \log K_{acid} - \frac{1}{2} \log c_{acid}$$

But $-\log [H^+]$ is the pH of our solution. Similarly, $-\log K$ is denoted by pK, known as the *dissociation exponent* of the acid. With these symbols we have

$$pH = \frac{1}{2} pK_{acid} - \frac{1}{2} \log c_{acid} \qquad (2)$$

We now use this equation to calculate the pH of a 0.1 *N* solution of formic acid, HCOOH ($K = 1.77 \times 10^{-4}$). We first calculate pK:

$$pK_{HCOOH} = -\log 1.77 \times 10^{-4} = -(0.25 - 4) = 3.75$$

Consequently

$$pH = 1.87 - \frac{1}{2} \log 0.1 = 1.87 + 0.5 = 2.37$$

Similarly, we find pH = 2.86 for 0.1 *N* acetic acid solution ($K = 1.86 \times 10^{-5}$), etc.

Let us now calculate the pH of a saturated (0.1 *M*) solution of H_2S. Hydrogen sulphide dissociates predominantly according to the equation

$$H_2S \rightleftarrows H^+ + HS^- \quad (K_1 = 5.7 \times 10^{-8})$$

The second stage of dissociation is so slight that it may be disregarded for the present purpose. Therefore we can use the equation derived above for calculating the pH. Substituting the numerical values of K and c into it, we have:

$$pK_{H_2S} = -\log 5.7 \times 10^{-8} = -(0.76-8) = 7.24$$

$$pH = 3.62 - \frac{1}{2}\log 0.1 = 3.62 + 0.5 = 4.12$$

Example 7. Derive a formula for calculating the pH of solutions of weak bases and use it to calculate the pH of a 0.1 N NH_4OH solution ($K = 1.79 \times \times 10^{-5}$).

Solution. Starting with the equation for the dissociation constant of a weak base and reasoning as in Example 6, we have the formula

$$pOH = \frac{1}{2}pK_{base} - \frac{1}{2}\log c_{base}$$

Hence

$$pH = 14 - \frac{1}{2}pK_{base} + \frac{1}{2}\log c_{base} \qquad (3)$$

For 0.1 N ammonia solution we have:

$$pK_{NH_4OH} = -\log 1.79 \times 10^{-5} = -(0.25-5) = 4.75$$

$$pH = 14 - 2.37 + \frac{1}{2}\log 0.1 = 11.13$$

In similar calculations the values of pK need not be calculated; they are given in Appendix III.

16. Buffer Systems

If we dissolve 0.01 mole of HCl in 1 litre of pure water, the H^+ ion concentration in the resultant 0.01 N hydrochloric acid solution is 1×10^{-2} g-ion/litre. The pH therefore drops from 7 to about 2.

In the same way it is easy to show (do this) that when 0.01 mole of NaOH is dissolved in 1 litre of water the pH rises from 7 to about 12. Thus, the pH of water is altered very sharply by the introduction of even relatively small amounts of acid or alkali.

Similar changes of pH occur if solutions of NaCl, KNO_3, $CaCl_2$, etc., are used instead of water. Very sharp changes of pH also result from additions of small amounts of acid or alkali to *very dilute* acid or alkali solutions. For example, if 0.01 mole of HCl is added to 1 litre of 10^{-5} M HCl solution, having pH = 5, the total concentration of acid in solution becomes $10^{-5} + 10^{-2} \approx 10^{-2}$ M and the pH falls by 3 units to a value of 2. When 0.01 mole of NaOH is added to 1 litre of 10^{-5} M HCl solution, the NaOH concentration* in the solu-

* 10^{-5} mole of HCl is neutralized by 10^{-5} mole of NaOH; therefore to find the concentration of the residual excess alkali in solution we must subtract the amount expended for neutralization (10^{-5} mole) from the total amount (10^{-2} mole).

tion becomes $10^{-2}—10^{-5} \approx 10^{-2}$ *M*. Therefore the pOH of this solution is 2, and pH = 12. This means that addition of caustic soda changes the solution pH by no less than 7 units.

Quite different variations of pH result when small amounts of acid or alkali are added to a mixture of a weak acid and a salt of that acid. If we add 0.01 mole of HCl to 1 litre of a mixture containing, for example, 0.1 *M* concentrations of CH_3COOH and CH_3COONa, the H^+ ion concentration is not increased as much as in the cases discussed above; in the present instance the hydrogen ions do not remain free but combine to a great extent with CH_3COO^- ions of the salt to give undissociated CH_3COOH molecules. Therefore the pH of the solution is altered to only a small extent. Calculation (see Example 1 below) shows that the pH falls by only 0.09, from 4.73 to 4.64, whereas in the case of pure water the fall is enormous, amounting to 5 units.

If we add 0.01 mole of a strong alkali to 1 litre of the same mixture, the OH^- ions at once combine with the H^+ ions of acetic acid. However, the concentration of the hydrogen ions is not altered substantially, as the loss is immediately made up by further dissociation of CH_3COOH; therefore in this case the solution pH changes little (it rises from 4.73 to 4.82).

Finally, suppose that we dilute the solution a hundredfold. It might seem that because of the great decrease of acetic acid concentration the H^+ ion concentration must also show a large decrease. However, we must not forget that the degree of dissociation of CH_3COOH increases in roughly the same proportion as the degree of dilution, because the concentration of CH_3COONa, which suppresses the dissociation of CH_3COOH by its common ion (CH_3COO^-), is also reduced a hundredfold.

Therefore *the presence of a mixture of a weak acid and its salt in a solution has the effect of regulating the* H^+ *ion concentration, reducing the influence of any factors which tend to alter the solution* pH. Such mixtures are known as *buffer solutions* or *buffer mixtures.*

Buffer mixtures also include mixtures of weak bases with their salts, such as $NH_4OH + NH_4Cl$, and mixtures of acid salts of different basicities. Examples are $NaH_2PO_4 + Na_2HPO_4$, $NaHCO_3 + Na_2CO_3$, etc.

Finally, solutions of strong acids and alkalies have a buffer effect at high enough concentrations. Of course, in this case the mechanism of the buffer action is entirely different. If the acid or alkali concentration is high, relatively large amounts must be added to produce an appreciable change of pH. Additions of small amounts of acid or alkali have practically no effect on the pH. For example, if we add 0.01 mole of NaOH to 1 litre of 0.1 *M* HCl solution, the H^+ ion concentration is lowered to 0.1—0.01 = 0.09 g-ion/litre. The pH is thus raised from 1 to 1.05, or by only 0.05 unit.

Buffer mixtures play a very important part in living organisms by maintaining constant the pH of the blood, lymph, etc.

Buffer mixtures often have to be used in analysis, in cases when an analytical operation (such as ion separation) has to be carried out at a definite and unchanging H^+ ion concentration. For example, in the separation of Ba^{++} in chromate form from Sr^{++} it is very important to maintain the solution pH constant at about 5, because at higher acidities the precipitation of Ba^{++} is incomplete and at lower acidities Sr^{++} is also precipitated. To avoid these complications, Ba^{++} is precipitated from acetic acid solution in the presence of sodium acetate, i.e., with the aid of the $CH_3COOH + CH_3COONa$ buffer mixture to maintain the required pH. Similarly, in the precipitation of Group II cations by ammonium carbonate and of Mg^{++} by sodium phosphate the $NH_4OH + NH_4Cl$ buffer mixture is used to give pH $\approx$ $\approx$ 8-9, as magnesium hydroxide is not precipitated at that pH.

Buffer mixtures are also used in experimental determinations of solution pH. It is not possible here to discuss the subject more fully, but we must note that determinations of solution pH are of very great importance, because the course of various chemical, biological, technological, and other processes depends to a very great extent on the H^+ ion concentration.

It is easy to calculate theoretically the pH of a given buffer mixture.

1. Mixtures of weak acids and their salts. Consider a mixture of a weak acid, CH_3COOH, with its salt CH_3COONa. The hydrogen ion concentration $[H^+]$ is found from the equation for the dissociation constant of acetic acid:

$$[H^+] = K \cdot \frac{[CH_3COOH]}{[CH_3COO^-]}$$

But CH_3COOH is a weak acid and is present in solution almost entirely in the form of undissociated molecules. Therefore the concentration of the latter may be taken as equal to the total acid concentration, i.e., $[CH_3COOH] \approx c_{acid}$.

However, the salt CH_3COONa is completely dissociated, while the dissociation of the acid CH_3COOH is very slight; therefore nearly all the CH_3COO^- anions present in solution originate from the dissociation of the salt. Since each dissociated salt molecule yields one CH_3COO^- ion, evidently $[CH_3COO^-] \approx c_{salt}$.

Accordingly, we have from the above equation

$$[H^+] = K \cdot \frac{c_{acid}}{c_{salt}} \qquad (1)$$

Taking logarithms and reversing the signs, we have

$$-\log [H^+] = -\log K - \log \frac{c_{acid}}{c_{salt}}$$

or

$$\mathrm{pH} = \mathrm{p}K - \log \frac{c_{acid}}{c_{salt}} \qquad (2)$$

where $\mathrm{p}K = -\log K$ is the dissociation exponent of the acid (see p. 71).

2. Mixtures of weak bases and their salts. An example is $NH_4OH + NH_4Cl$. In this case from the equation for the dissociation constant of NH_4OH we have

$$[OH^-] = K \cdot \frac{[NH_4OH]}{[NH_4^+]} = K \cdot \frac{c_{base}}{c_{salt}}$$

Reasoning as before, we find

$$\mathrm{pOH} = \mathrm{p}K - \log \frac{c_{base}}{c_{salt}}$$

But it was shown in Sec. 15 that pH + pOH = 14. Therefore

$$\mathrm{pH} = 14 - \mathrm{pOH} = 14 - \mathrm{p}K + \log \frac{c_{base}}{c_{salt}} \qquad (3)$$

The following examples illustrate the use of these formulas.

Example 1. Calculate the pH of a $CH_3COOH + CH_3COONa$ buffer mixture containing 0.1 mole of each. Find the change of pH produced in 1 litre of the mixture by addition of (a) 0.01 mole of HCl; (b) 0.01 mole of NaOH; (c) by hundredfold dilution.

Solution. For acetic acid $\mathrm{p}K = 4.73$ (see Appendix III); therefore

$$\mathrm{pH} = 4.73 - \log \frac{0.1}{0.1} = 4.73$$

When 0.01 mole of HCl is added to 1 litre of this mixture, 0.01 mole of CH_3COONa is converted into the same molar amount of CH_3COOH. Therefore

$$\mathrm{pH} = 4.73 - \log \frac{0.11}{0.09} = 4.64$$

Similarly, when 0.01 mole of NaOH is added to 1 litre of the solution the same molar amount of CH_3COOH is converted into CH_3COONa and we have

$$\mathrm{pH} = 4.73 - \log \frac{0.09}{0.11} = 4.82$$

Finally, on hundredfold dilution of the mixture

$$\mathrm{pH} = 4.73 - \log \frac{0.001}{0.001} = 4.73$$

Thus, calculations with the aid of Eq. (2) confirm that buffer mixtures maintain nearly constant pH values on addition of small amounts of acids or alkalies, or on dilution*.

Example 2. Find the pH of an $NH_4OH + NH_4Cl$ buffer mixture containing 0.1 mole of each. Calculate the change of pH: (a) on addition of 0.01 mole of HCl to 1 litre of the mixture; (b) on addition of 0.01 mole of NaOH to 1 litre of the mixture; (c) on tenfold dilution of the mixture with water.

Solution. Reasoning as before, we have

$$pH = 14 - 4.75 + \log \frac{0.1}{0.1} = 9.25$$

On addition of 0.01 mole of HCl c_{base} falls to 0.09 *M*, and c_{salt} rises to 0.11 *M*.

Therefore

$$pH = 14 - 4.75 + \log \frac{0.09}{0.11} = 9.16$$

On addition of 0.01 mole of NaOH to 1 litre of the mixture we have

$$pH = 14 - 4.75 + \log \frac{0.11}{0.09} = 9.34$$

Finally, on tenfold dilution of the solution we have**

$$pH = 14 - 4.75 + \log \frac{0.01}{0.01} = 9.25$$

Example 3. Find the change of pH of a $CH_3COOH + CH_3COONa$ mixture as the result of tenfold increases in the concentrations of (a) CH_3COOH; (b) CH_3COONa.

Solution. We saw in Example 1 that at equal concentrations of the acid and the salt the pH of the mixture is equal to p*K* of the acid, i.e., 4.73. Now suppose that the CH_3COOH concentration in the mixture is increased tenfold, to 1 *M*.

---

* In accordance with what was said on p. 69 the following formula should be used for more precise calculations of pH values of buffer mixtures:

$$pH = -\log a_{H^+} = -\log [H^+] \cdot f_{H^+}$$

The method for calculating ion activities in mixtures of weak acids with their salts was demonstrated in the example in Sec. 14. The value of a_{H^+} is found and pH is obtained from it by the usual method. For example, the activity of hydrogen ions in a solution containing 0.1 mole CH_3COOH and 0.05 mole CH_3COONa per litre was found to be 4.3×10^{-5}. Therefore

$$pH = -\log 4.3 \times 10^{-5} = -(0.63 - 5) = 4.37$$

Calculation with the approximate Equation (2) gives pH = 4.43.

** According to Examples 1 and 2, the pH of a buffer mixture should not change on dilution. However, in practice it does change somewhat because the ionic strength of the solution is decreased by dilution and the activity coefficients of the ions alter accordingly. If the activity coefficients are taken into account, the pH changes on dilution can be calculated. For instance, in Example 2 the pH increases by about 0.07 unit.

Then

$$pH = 4.73 - \log \frac{1}{0.1} = 4.73 - \log 10 = 4.73 - 1 = 3.73$$

When the salt concentration is increased tenfold, we have

$$pH = 4.73 - \log \frac{0.1}{1} = 4.73 + 1 = 5.73$$

In the case of a NH_4OH + NH_4Cl mixture it is also easy to show that a tenfold increase of the NH_4OH concentration raises the pH by one unit, and a corresponding increase of the NH_4Cl concentration lowers it by the same amount.

The ability of buffer mixtures to maintain almost constant pH values is based on the fact that their individual components combine with the H^+ or OH^- ions of acids or bases added to the solution (or formed as the result of reactions). Of course, this ability has a limit which depends on the concentrations of the components in the buffer mixture. For example, if more than 0.1 mole of HCl or NaOH is added to 1 litre of 0.1 *N* ammonium buffer mixture (i.e., a mixture containing NH_4OH + NH_4Cl at 0.1 *N* concentrations), a very large change of pH is produced in either case, because the amounts of NH_4OH or NH_4Cl available are not sufficient to combine with the H^+ or OH^- ions. An excess of the added strong acid or alkali remains in solution, and the pH alters sharply.

Calculations from Equation (3) (p. 75) and experiments show that the pH begins to alter considerably long before the corresponding component of the buffer mixture has been completely used up in the reaction. This is illustrated by the data in Table 8.

Table 8 leads to the following conclusions, very important for analysis.

1. Every buffer mixture maintains a practically constant pH value only up to a certain limiting amount of added acid or alkali; i.e., it has a definite *buffer capacity*. For example, if we want to maintain the pH constant to within 0.5 unit, not more than 0.05 mole of acid or alkali may be added to 1 litre of 0.1 *N* buffer mixture.

2. The higher the concentrations of the components of a buffer mixture, the greater its buffer capacity. Comparison of the values for the two buffer mixtures shows that 1 *N* ammonium buffer mixture is much more effective than the 0.1 *N* mixture in maintaining constant pH. For example, with the 1 *N* buffer mixture a pH change of $\sim$ 0.5 unit is produced only on addition of 0.5 mole of HCl or NaOH per litre of solution; addition of 0.05 mole of either of these substances alters the pH by only 0.03 unit, whereas in the case of 0.1 *N* buffer mixture the corresponding change is 0.48 unit.

3. The resistance of a buffer solution to pH changes gradually diminishes with increasing additions of acid or alkali.

Table 8

Effect of Added Alkali or Acid on the pH of Ammonium Buffer Mixtures

NaOH added, mole/litre	pH		HCl added, mole/litre	pH	
	0.1 *N* buffer mixture	1 *N* buffer mixture		0.1 *N* buffer mixture	1 *N* buffer mixture
—	9.25	9.25	—	9.25	9.25
0.01	9.34	9.26	0.01	9.16	9.24
0.02	9.42	9.27	0.02	9.08	9.23
0.05	9.73	9.29	0.05	8.77	9.21
0.10	11.13	9.34	0.10	5.13	9.16
0.50	13.60	9.73	0.50	0.40	8.77
1.00	13.95	11.13	1.00	0.05	5.13

For example, the average changes of pH produced by additions of 0.01 mole of NaOH or HCl to 1 litre of 0.1 *N* buffer mixtures are:

in the 0.00-0.02 mole range . . 0.09 pH unit
in the 0.02-0.05 mole range . . 0.10 pH unit
in the 0.05-0.10 mole range . . 0.28 pH unit

The capacities of buffer mixtures must be taken into account when they are used in analysis. For example, if we want to conduct a reaction, which gives rise to H^+ ions, at practically constant pH it is not sufficient merely to add a buffer mixture of the required pH to the solution; its buffer capacity must be adequate, otherwise the solution pH will not remain constant. In other words, the components of the buffer mixture must be present in suitable and sufficiently high concentrations.

Buffer mixtures are widely used in analytical practice for various reactions.

The following buffer mixtures are the most commonly used*.

Mixture	*Composition*	pH
Formate	Formic acid, HCOOH, and sodium formate, HCOONa	3.7
Benzoate	Benzoic acid, C_6H_5COOH, and sodium benzoate, C_6H_5COONa	4.2
Acetate	Acetic acid, CH_3COOH, and sodium acetate, CH_3COONa	4.7
Phosphate	Sodium dihydrogen phosphate, NaH_2PO_4, and disodium hydrogen phosphate, Na_2HPO_4	6.8
Ammonium	Ammonia, NH_4OH, and ammonium chloride, NH_4Cl .	9.2

* The pH values refer to equal concentrations of the two components.

It is possible, in accordance with Eqs. (2) and (3) (p. 75), to alter the pH by varying the concentrations of the components of buffer mixtures. The concentration of one of the components should not be more than ten times that of the other to ensure that the change of the buffer capacity is not too great, i.e., that the action of the buffer should remain effective. Since a tenfold change of one of the concentrations changes the pH by one unit (see Example 3 above), it is evident that the effective range of buffer mixtures extends by one pH unit on either side of the values given above. For example, it is possible to prepare various $NH_4OH + NH_4Cl$ buffer mixtures for maintaining the pH between 8.2 (with 10 times as much NH_4Cl as NH_4OH) and 10.2 (with a tenfold excess of NH_4OH).

The effective range of acetate buffer mixture is pH = 3.7-5.7, etc.

17. Determination of pH in the Course of Qualitative Analysis

Since the pH of the medium is important in most analytical reactions, it often has to be determined practically in the course of analysis. There are various methods for pH determination. The more accurate methods are rather complicated and require special apparatus; they are therefore unsuitable for qualitative analysis, where the accuracy is not closer than one pH unit or may often be even lower. Accordingly, colorimetric methods only are used for such purposes; these are based on the use of reagents which alter colour in accordance with the hydrogen ion concentration. These reagents (such as litmus) are known as *acid-base indicators.* They are weak organic acids or bases with undissociated molecules differing in colour from their ions*. Litmus contains the so-called azolitmic acid, with red undissociated molecules yielding blue anions.

If we denote any indicator acid by HInd and its anion by Ind^-, he dissociation of litmus in solution may be represented as follows:

$$\underset{\text{Red}}{HInd} \rightleftarrows \underset{\text{Blue}}{H^+ + Ind^-}$$

When litmus is dissolved in water (or in any neutral solution), its HInd molecules and the simultaneously present Ind^- anions confer an intermediate (violet) colour on the solution. If a small amount of any acid is added, the equilibrium is shifted to the left. In other words, the H^+ ions introduced with the acid combine with nearly all the Ind^- anions present in solution to give undissociated HInd molecules, and the solution turns red. If an alkali is added to a neutral litmus solution, its OH^- ions combine with the H^+ ions of the indi-

* Because of differences in structure.

cator to give undissociated H_2O molecules. As a result, the dissociation equilibrium of the indicator is shifted to the right, towards the formation of more Ind^- anions, and the solution turns blue.

Colour changes of other indicators are explained analogously. For example, phenolphthalein has colourless undissociated molecules while the anions are red:

$$\underset{\text{Colourless}}{HInd} \rightleftarrows \underset{\text{Red}}{H^+ + Ind^-}$$

Therefore phenolphthalein should become red with alkalies and colourless with acids.

The addition of an acid or alkali obviously alters the pH of the solution, and the colour changes of these indicators are associated with this change. Detailed studies showed that the colour change occurs within certain pH limits characteristic for each indicator, or its pH *range*. For example, at any pH value below 5 litmus has the same red colour. Above pH = 5 the colour begins to change appreciably and becomes bright blue at pH = 8. No matter how much the pH is raised further, i.e., no matter how much more alkali is added to the solution, the colour remains the same blue as at pH = = 8. The pH range of litmus is therefore 5-8. Other indicators have other pH ranges*. For example, the range of phenolphthalein is pH = = 8-10; at $pH < 8$ this indicator is colourless and at $pH \geqslant 10$ it has an intense red colour. Within the range the originally colourless solution becomes progressively redder, reaching maximum intensity at pH = 10.

The simplest method of determining the reaction of a solution is to test it with litmus solution or litmus paper. Litmus paper consists of strips of filter paper impregnated with litmus solution coloured by a very small amount of acid (red litmus paper) or alkali (blue litmus paper) and dried. If a drop of solution turns blue litmus paper red, the solution is acid ($pH < 5$). A solution having an alkaline reaction ($pH \geqslant 8$) turns red litmus blue. If neither paper changes colour by the action of an unknown solution, the latter is regarded as neutral ($pH \approx 7$).

Such approximate determinations of the reaction of solutions are often sufficient. However, in a number of cases it is very important to have a more accurate idea of the pH of a solution. This can be obtained with the aid of several different indicators having different pH ranges.

---

* This depends on the dissociation constants of the various indicator acids (or bases).

In addition to litmus, the following indicators can be used for pH determination:

Thymol blue (pH=1.2-2.8; red to yellow)
Thymol blue (pH=8.0-9.6; yellow to blue)*
Methyl orange (pH=3.1-4.4; pink to orange)**
Methyl red (pH=4.4-6.2; red to yellow)
Phenol red (pH=6.8-8.0; yellow to red)
Phenolphthalein (pH=8.0-10.0; colourless to red)

In addition to these five indicators, the following two may also be used:

Methyl violet (pH=0.2; green to violet; blue at pH=1)
Thymolphthalein (pH=9.3-10.5; colourless to blue)

It is not difficult to determine the approximate pH of a solution (with sufficient accuracy for qualitative analysis) by comparing its effects on different indicators (or on papers impregnated with their solutions).

For example, suppose that the following colours were obtained when drops of an unknown solution were mixed with drops of indicator solutions on a spot plate:

Indicator	*Colour*
Thymol blue	yellow
Methyl orange	orange (or yellow)
Methyl red	yellow
Phenol red	yellow
Phenolphthalein	colourless

The following conclusions may be drawn from these results.

The yellow colour of thymol blue shows that the solution pH is in the range of 2.8-8.0. As no red colour is produced with phenolphthalein, this confirms that the pH does not exceed 8.0. The orange colour of methyl orange shows that pH $\geqslant$ 4.4, and the yellow colour of methyl red indicates that pH $\geqslant$ 6.2. However, since phenol red was turned yellow, the pH must be below 6.8. Therefore the pH must be in the range of 6.2-6.8, or approximately 6.5. It can be seen that it is not always necessary to use all the indicators. For example, in the present case tests with methyl orange and phenolphthalein

* Thymol blue has two ranges. At pH = 1.2 and lower it is red; at pH = 2.8 it turns yellow and retains that colour up to pH = 8.0. On further rise of pH the indicator gradually turns bluer and remains blue from pH = 9.6 upwards.

** At low concentrations of the indicator, the colour of methyl orange is yellow at pH $\geqslant$ 4.4.

are unnecessary. It is preferable to start the tests with thymol blue. because a red colour ($pH \ll 1.2$, strongly acidic solution) or a blue colour ($pH \geqslant 9.6$, strongly alkaline solution) would make further testing superfluous.

If an indicator gives a colour between the extremes of its range. this means that the pH of the solution lies within the range of that indicator. For example, if thymol blue gives a green colour, formed by optical addition of yellow and blue, we may conclude that the pH is intermediate between 8.0 and 9.6, i.e., about 9. The same inference follows if phenolphthalein gives a pale-pink colour rather than bright red.

Instead of solutions, we can use the corresponding indicator papers and apply small amounts of the unknown solution to them with a glass rod, observing the colour formed. However, the colours obtained are less bright and alter somewhat owing to adsorption of solutes by the paper.

Instead of the range of indicators described above, it is convenient to use the so-called universal indicators, which are indicator mixtures changing colour over a wide range of pH.

For example, Kolthoff's universal indicator (produced by the Soviet reagent industry) is a mixture of five different indicators which changes colour in the pH range from 2 to 10 as follows:

pH	*Colour*	pH	*Colour*
2 (and below)	red-pink	7	yellow-green
3	red-orange	8	green
4	orange	9	blue-green
5	yellow-orange	10 (and above)	violet
6 . . .	lemon-yellow		

The indicator may be used either in the form of solution, a drop being mixed in a small porcelain basin with 1-3 drops of the unknown solution, or in the form of indicator paper* impregnated with the universal indicator solution and dried. A colour scale is supplied with the paper, showing the colour produced at different pH values. The scale makes pH determination very much easier. In absence of a scale it is useful to have a series of buffer solutions, testing them with the universal indicator at the same time as the unknown solution**.

With the aid of more complicated techniques it is possible to determine the pH of solutions colorimetrically to within about 0.2 pH

---

* The Riga Laboratory of the D. I. Mendeleyev All-Union Chemical Society sells universal indicator paper for the pH range 1-10.

** Fuller details on the composition and preparation of the universal indicator and on the preparation of other indicator solutions are given in Appendix VII.

unit. The procedure used is described in textbooks of quantitative analysis.

When the results of pH determinations are interpreted, it must be taken into account that the distilled water used for preparing the solutions is not absolutely pure; it contains CO_2 absorbed from the air and substances extracted from the glass of the containers, such as Na_2SiO_3. Therefore the experimental pH value of distilled water does not agree with the theoretical value of 7, but is usually somewhat lower (5-6). If this water is used for preparing solutions of neutral salts such as NaCl, KNO_3, etc., the pH of the solutions is not 7 but that of the water (i.e., 5-6).

If strictly neutral solutions of these salts are required, it is necessary to use either water neutralized to pH = 7 or water freed from CO_2 by prolonged boiling. To prevent re-absorption of CO_2 on cooling, after boiling the vessel is closed with a stopper through which is passed a tube containing soda lime (calcined mixture of NaOH and CaO). When air passes through this tube the CO_2 in it is absorbed by the NaOH and CaO to form the solid compounds Na_2CO_3 and $CaCO_3$. Solutions of salts should be similarly protected from CO_2 to keep their pH at the theoretical value of 7. It should also be remembered that the pH of a solution may rise during prolonged storage because of extraction of soluble silicates from the glass by water; these silicates have an alkaline reaction owing to hydrolysis. To prevent this, container walls are coated inside with paraffin wax.

All these precautions, which complicate work considerably, rarely have to be taken in practice, because in most cases they do not result in any special advantage. One should merely remember that for the reasons given the pH of neutral solutions determined experimentally may not agree with the theoretical pH = 7.

QUESTIONS AND PROBLEMS

1. Find the concentrations of H_2 and CO_2 at which equilibrium becomes established in the reversible reaction $CO + H_2O \rightleftarrows H_2 + CO_2$, if the initial concentration of CO_2 and H_2O vapour are 1 mole and 10 moles per litre. Calculate the percentage of CO converted into CO_2 ($K = 1$).

Answer. $\sim 0.9\ M$; 90%.

2. State in which direction the equilibrium in the reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$ is shifted if the concentration of (a) hydrogen and (b) ammonia in the gas mixture is increased.

3. Is the equilibrium in the above reactions influenced by compression of the gas mixture to half the initial volume? If so, in which direction is the equilibrium shifted?

4. Calculate the degree of dissociation of formic acid in 0.5 *N* solution, given that the H^+ ion concentration is 0.01 g-ion/litre.

Answer. $\alpha = 0.02$ (2%).

5. When a solution of hydrocyanic acid, HCN, is diluted with water, do the degree of dissociation and the dissociation constant of the acid alter?

6. From the data of Problem 4 calculate the dissociation constant of formic acid and calculate its degree of dissociation in 1 N solution.

Answer. $K = \sim 2 \times 10^{-4}$; $\alpha = 0.014$ (1.4%).

7. Find the OH^- ion concentration in a 0.05 N NH_4OH solution ($K = 1.8 \times 10^{-5}$) containing 0.1 mole NH_4Cl per litre. How much does the presence of NH_4Cl lower this concentration? An approximate calculation is required, disregarding the activity coefficients of the ions.

Answer. $[OH^-] = 9 \times 10^{-6}$ g-ion/litre; in the presence of 0.1 mole NH_4Cl per litre the OH^- concentration is reduced by a factor of about 105.

8. Find the ionic strengths of solutions containing, per litre:

(a) 0.1 mole KCl; (b) 0.1 mole K_2SO_4; (c) 0.1 mole $MgSO_4$; (d) 0.1 mole $AlCl_3$; (e) 0.01 mole $K_2SO_4 + 0.01$ mole $Al_2(SO_4)_3$.

Answer. (a) 0.1; (b) 0.3; (c) 0.4; (d) 0.6; (e) 0.18.

9. Calculate the activities of Ca^{++} and Cl^- ions in 0.02 N $CaCl_2$ solution.

Answer. $a_{Ca^{++}} = 0.0054$; $a_{Cl^-} = 0.0172$.

Note. To solve this problem, first calculate the ionic strength of the solution and then find the activity coefficients of Ca^{++} and Cl^- ions from the data of Table 6 by interpolation.

10. Find the OH^- ion activity in 0.05 N NH_4OH solution which also contains NH_4Cl at 0.1 N concentration, and compare the result with the activity of the same ions in the absence of the ammonium salt. What is the influence of the ammonium salt on a_{OH^-}? Compare the result with the value found by approximate calculation (see Problem 7).

Answer. $a_{OH^-} = 1.15 \times 10^{-5}$; the presence of the ammonium salt in 0.1 N concentration lowers a_{OH^-} by a factor of about 82.

Note. The (thermodynamic) dissociation constant of NH_4OH is to be taken as 1.8×10^{-5}; the activity coefficients of the ions formed by dissociation of ammonium hydroxide in the absence of NH_4Cl are to be taken as unity.

11. Find the pH of solutions containing: (a) 2×10^{-4} g-ion H^+ per litre; (b) 0.008 g-ion OH^- per litre.

Answer. (a) 3.7; (b) 11.9.

12. Two solutions have the following pH values: (a) 2.63; (b) 12.45. Find their H^+ and OH^- ion concentrations.

Answer. (a) $[H^+] = 2.34 \times 10^{-3}$; $[OH^-] = 4.27 \times 10^{-12}$; (b) $[H^+] = 3.54 \times 10^{-13}$; $[OH^-] = 2.82 \times 10^{-2}$.

13. Calculate the pH of (a) 0.005 N HCl solution; (b) 0.015 N KOH solution.

Answer. (a) 2.30; (b) 12.18.

14. Calculate the pH of (a) 0.02 N CH_3COOH solution; (b) saturated (at 20°) 3.8×10^{-2} M CO_2 solution; (c) 0.05 N NH_4OH solution.

Answer. (a) 3.22; (b) 3.89; (c) 10.98.

15. What is the effect of hundredfold dilution with water on the pH of HCl and KOH solutions?

16. Find the changes in the pH of a solution containing 10^{-5} N NaOH resulting from the addition of (a) 0.001 mole NaOH and (b) 0.001 mole HCl to one litre of the solution.

Answer. (a) increased by ~2; (b) decreased by ~6.

17. A solution contains 0.056 mole NH_4OH and 0.1 mole NH_4Cl per litre. Find the pH of the solution and the change resulting from the addition of (a) 0.001 mole NaOH and (b) 0.001 mole HCl to one litre of the solution (compare the result with the previous answer).

Answer. pH = 9.00; (a) increased by 0.01; (b) decreased by 0.01.

18. Calculate the pH of buffer mixtures containing (a) 0.01 M CH_3COOH and 0.01 M CH_3COOK; (b) 0.01 M CH_3COOH and 0.5 M CH_3COOK; (c) 0.5 M CH_3COOH and 0.01 M CH_3COOK.

Answer. (a) 4.73; (b) 6.43; (c) 3.03.

19. To prepare a formate buffer mixture, 100 ml of 23 *N* formic acid solution was mixed with 3 ml of 15 *N* NH_4OH solution. Calculate the pH of the mixture.

Answer. pH = 2.05.

20. What changes are produced in the pH values of (a) 0.2 *N* acetate buffer mixture and (b) 0.1 *N* acetate buffer mixture by additions of 0.05 mole of HCl and NaOH respectively to 1 litre of mixture?

Answer. (a) decreased by 0.22 with HCl, increased by the same amount with NaOH; (b) decreased by 0.48 with HCl, increased by the same amount with NaOH.

21. What conclusions may be drawn from the answers to Problem 20 about the relative buffer capacities of 0.2 *N* and 0.1 *N* acetate buffer mixtures?

22. Find the ratio of the concentrations of free formic acid, HCOOH, and its salt, HCOONa, in a formate buffer mixture to give a pH of 2.25. Would this buffer mixture be sufficiently effective?

Answer. $c_{acid} : c_{salt} = 31.6$.

23. Find the volume (in ml) of 0.5 *N* CH_3COONa which must be added to 100 ml of 2 *N* CH_3COOH to give a buffer mixture of pH = 4.0.

Answer. ~74.5 ml.

REACTIONS AND ANALYTICAL PROCEDURE FOR GROUP I CATIONS

18. General Characteristics of Group I Cations

Cation Group I includes ions of the metals potassium, sodium and magnesium, the ammonium ion NH_4^+, etc. Most of their salts are readily soluble in water. The solubility of their sulphides, hydroxides, carbonates and chlorides in water is especially important for analysis, as this distinguishes Group I from all the other groups (see Table 2, p. 32).

Owing to the solubility of these salts, Group I cations are not precipitated by the other group reagents, i.e., HCl, H_2S, $(NH_4)_2S$ and $(NH_4)_2CO_3$, and remain in solution when cations of the other groups are separated as insoluble salts. There is no group reagent which precipitates all four cations of Group I. As cations of the other groups interfere with the detection of K^+, Na^+ and Mg^{++} ions, in systematic analysis these ions are detected only after all other cations have been completely removed from solution.

The metals potassium and sodium belong to Group I of the periodic system and are active alkali metals. They decompose water rapidly even at room temperature with liberation of hydrogen and formation of the hydroxides, for example

$$2Na + 2H_2O = 2NaOH + H_2\uparrow$$

These are the strongest alkalies. They are almost completely ionized in aqueous solution. Therefore sodium and potassium salts of strong acids are not hydrolyzed* and their solutions have a neutral

* The hydrolysis of salts is discussed in Sections 43 and 44.

reaction; this means that the pH of these solutions is determined by the pH of the water used for their preparation (see p. 83). The potassium and sodium salts of weak acids are hydrolyzed to a considerable degree, and their solutions are alkaline (pH > 7).

Ammonium hydroxide, NH_4OH (usually referred to as ammonia for short), is a weak alkali. Its degree of dissociation in 1 *N* solution is about 0.4%. Solutions of ammonium salts of strong acids therefore have an acid reaction (pH < 7). For example, the pH of 1 *N* NH_4Cl solution is 4.6.

The K^+, Na^+ and Mg^{++} cations (and also Li^+, Rb^+ and Cs^+, which belong to cation Group I) have completed shells of eight or two electrons, similar to the shells of atoms of the inert gases. The Mg^{++} ion differs from the other Group I cations; it belongs to Group II of the periodic system and is intermediate between analytical Groups I and II, so that it can be included in either. The Mg^{++} cation resembles Group II cations in that its basic carbonate* $(MgOH)_2CO_3$ is sparingly soluble in water. However, it is soluble in ammonium salts, and since Group II is precipitated by ammonium carbonate in the presence of NH_4Cl, the Mg^{++} ion remains in solution with Group I, and is not precipitated with Group II. It is therefore more conveniently studied with Group I.

All the Group I cations are colourless in aqueous solution.

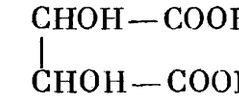
19. Reactions of the K^+ Cation

There are very few precipitation reactions for detection of the K^+ cations. The most important ones are described below.

1. Tartaric acid, $H_2C_4H_4O_6$, and its acid sodium salt, sodium hydrogen tartrate ($NaHC_4H_4O_6$) give a white crystalline precipitate of potassium hydrogen tartrate, $KHC_4H_4O_6$, with solutions of potassium salts. Let us consider this reaction in more detail. Tartaric acid is a relatively weak organic acid. Its molecule contains six hydrogen atoms, but only two can split off as H^+ ions, so that the acid is dibasic**. Accordingly, it can form both neutral and acid salts. The neutral potassium and sodium tartrates, $K_2C_4H_4O_6$ and $Na_2C_4H_4O_6$,

* Basic salts are compounds containing, in addition to metal ions and acid radicals (characteristic of neutral salts), hydroxyl groups characteristic of bases. Basic salts are usually formed by hydrolysis of neutral salts, e.g., $MgCl_2 + H_2O \rightleftarrows MgOHCl + HCl$. For fuller details see Sec. 43.

** This is due to the presence of two carboxyl groups (—COOH) in the tartaric acid molecule, as is evident from its structural formula



When such compounds dissociate, the hydrogen atoms present in the carboxyl groups are split off as ions.

and sodium hydrogen tartrate, $NaHC_4H_4O_6$, are readily soluble in water. On the other hand, the solubility of potassium hydrogen tartrate, $KHC_4H_4O_6$, is relatively low. The formation of this salt is used for detection of the K^+ ion. In the case of KCl the reaction is represented by the equation

$$KCl + NaHC_4H_4O_6 = \downarrow KHC_4H_4O_6 + NaCl$$

Other potassium salts react analogously; for example

$$K_2SO_4 + 2NaHC_4H_4O_6 = \downarrow 2KHC_4H_4O_6 + Na_2SO_4$$

Of course, this is to be expected, as only K^+ and $HC_4H_4O_6^-$ ions are involved in the reaction. Therefore the other ions may be omitted from the equation. We then have the ionic equation for the reaction:

$$K^+ + HC_4H_4O_6^- = KHC_4H_4O_6$$

Study this reaction experimentally as follows. Take about one-quarter of a test tube full of KCl solution and add roughly the same volume of the reagent ($NaHC_4H_4O_6$ solution). If a precipitate does not form, dip a glass rod into the liquid and rub the inside wall of the tube gently. The point is that supersaturated solutions are often formed as the result of reactions leading to the formation of sparingly soluble substances. Although such solutions contain solute in excess of the amount needed for saturation under the given conditions, they may remain for a long time without forming a precipitate. Rubbing, shaking, and similar mechanical action accelerate precipitate formation.

Having obtained a precipitate of $KHC_4H_4O_6$, study its properties; this is necessary for confirmatory tests and clarifies the conditions under which the test can be reproduced.

First confirm that the precipitate is crystalline. Close the top of the test tube, turn it upside down, and examine the small crystals of $KHC_4H_4O_6$ adhering to the bottom and sides. Amorphous precipitates (and also precipitates consisting of very fine crystals) readily separate from the glass under these conditions.

Test the effects of heating, acids, and alkalies on the precipitate. Shake the test tube and divide the contents between four other test tubes. Heat the first, add a strong alkali (NaOH or KOH) to the second, a strong acid such as HCl to the third, and a weak acid such as CH_3COOH to the fourth; in each case mix the contents of the tube. The precipitate dissolves in every case except the fourth. The reactions with strong acids and alkalies may be represented by the following equations:

$$KHC_4H_4O_6 + HCl = KCl + H_2C_4H_4O_6$$
$$KHC_4H_4O_6 + KOH = K_2C_4H_4O_6 + H_2O$$
$$KHC_4H_4O_6 + NaOH = KNaC_4H_4O_6 + H_2O$$

The $KHC_4H_4O_6$ *precipitate is therefore a white crystalline substance which is soluble in hot water and in strong acids and alkalies, but insoluble in weak acetic acid.* It should be noted that $KHC_4H_4O_6$ will dissolve in a large volume of cold water, and the sensitivity of this reaction is therefore relatively low (dilution limit 1 : 1,000). These properties of the precipitate determine the test conditions.

Consider, for example, whether $KHC_4H_4O_6$ would be precipitated from hot solution, from acid solution, or from alkaline solution. Check your conclusions by experiment. To do this, add a strong acid or alkali to a solution of a potassium salt and attempt to detect K^+ in the solution. Does the test work?

Evidently $KHC_4H_4O_6$ would not be precipitated and the test would again fail if the K^+ ion concentration in solution is low.

Summarizing the results of all these experiments, we can see that the following conditions must be satisfied for detection of K^+ with the aid of $NaHC_4H_4O_6$:

(a) *the concentration of the* K^+ *ion must be high enough*;

(b) *the test must be carried out in the cold*;

(c) *the unknown solution must have a neutral reaction.*

It may happen in the course of analysis that the conditions have to be adjusted for the reaction. For example, if the solution is too dilute, it is concentrated by evaporation of most of the water. If the solution is acid or alkaline, it is neutralized. Alkaline solutions may be neutralized by any of the acids available in the laboratory, preferably acetic, as an excess of this acid would not interfere with precipitation of $KHC_4H_4O_6$. Acid solutions must be neutralized by NaOH. It is obvious that KOH cannot be used for the purpose, as this would introduce the ion which is being sought.

As already stated, instead of $NaHC_4H_4O_6$ we can use tartaric acid, $H_2C_4H_4O_6$, for detection of K^+, because its first dissociation stage

$$H_2C_4H_4O_6 \rightleftarrows H^+ + HC_4H_4O_6^-$$

yields the $HC_4H_4O_6^-$ ion needed for the formation of potassium hydrogen tartrate. However, the reaction is then accompanied by the formation of a strong acid in solution, for example:

$$KCl + H_2C_4H_4O_6 \rightleftarrows KHC_4H_4O_6 + HCl$$

Since the $KHC_4H_4O_6$ precipitate is soluble in strong acids, the formation of an acid has an adverse effect by making the reaction reversible. To avoid this, the test with $H_2C_4H_4O_6$ is carried out in the presence of CH_3COONa; under these conditions the strong acid formed is replaced by a weak one, acetic, which does not dissolve the precipitate:

$$CH_3COONa + HCl = CH_3COOH + NaCl$$

We obtain the overall equation for the reaction by adding the two equations shown above:

$$KCl + H_2C_4H_4O_6 + CH_3COONa = \downarrow KHC_4H_4O_6 + NaCl + CH_3COOH$$

2. Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$, forms a yellow precipitate of $K_2Na[Co(NO_2)_6]$ with solutions of potassium salts. This reagent is a complex salt of trivalent cobalt which dissociates to yield $[Co(NO_2)_6]^{---}$ ions, and these react with K^+ and Na^+ ions:

$$2K^+ + Na^+ + [Co(NO_2)_6]^{---} = \downarrow K_2Na[Co(NO_2)_6]$$

Study this reaction experimentally, adding an equal volume of the reagent to a few drops of a solution of a potassium salt. If the precipitate does not form at once, leave the solution to stand. A distinct bright yellow precipitate is formed.

Alkalies interfere with the reaction, as they decompose the reagent with formation of a dark brown precipitate of $Co(OH)_3$:

$$Na_3[Co(NO_2)_6] + 3NaOH = \downarrow Co(OH)_3 + 6NaNO_2$$

The $K_2Na[Co(NO_2)_6]$ precipitate is much less soluble than $KHC_4H_4O_6$ in acids. However, if the solution is acidic it is advisable to add sodium acetate in order to replace the strong acid by a weak one.

This reaction is more sensitive than the reaction with $NaHC_4H_4O_6$ (dilution limit about 1 : 13,000). Therefore in practice this is the preferable test for detection of K^+. It must be remembered, however, that $Na_3[Co(NO_2)_6]$ decomposes fairly rapidly on standing and its brown colour changes to pink (colour of the Co^{++} ion). If the solution has turned pink, it is unsuitable for detection of K^+.

Iodide ions, introduced in systematic group analysis for reduction of AsO_4^{---} to AsO_3^{---}, interfere with the reaction as they cause decomposition of $Na_3[Co(NO_2)_6]$. Therefore if I^- ions are present the solution for detection of K^+ must be evaporated to dryness with 6 *N* HNO_3 solution, and the dry residue ignited gently. The iodide ions are oxidized by HNO_3 to form elemental iodine which volatilizes completely on evaporation. The dry residue is dissolved in water and tested for K^+ as described above.

3. Chloroplatinic acid, $H_2[PtCl_6]$, gives a yellow crystalline precipitate of potassium chloroplatinate with fairly concentrated solutions of potassium salts:

$$2K^+ + [PtCl_6]^{--} = \downarrow K_2[PtCl_6]$$

Viewed under the microscope, the crystals of the precipitate appear as octahedra. Similar precipitates are given by NH_4^+ (and also by Cs^+ and Rb^+).

4. Perchloric acid, $HClO_4$, gives a white precipitate of potassium perchlorate:

$$K^+ + ClO_4^- = \downarrow KClO_4$$

The precipitate becomes much more soluble on heating. The solubility can be greatly lowered by addition of ethyl alcohol.

5. **Microcrystalloscopic test.** Put a drop of a solution of a potassium salt on a glass slide and evaporate it to dryness by putting the slide on the edge of an electric hot plate (*not over the heating coil*)*. Cool

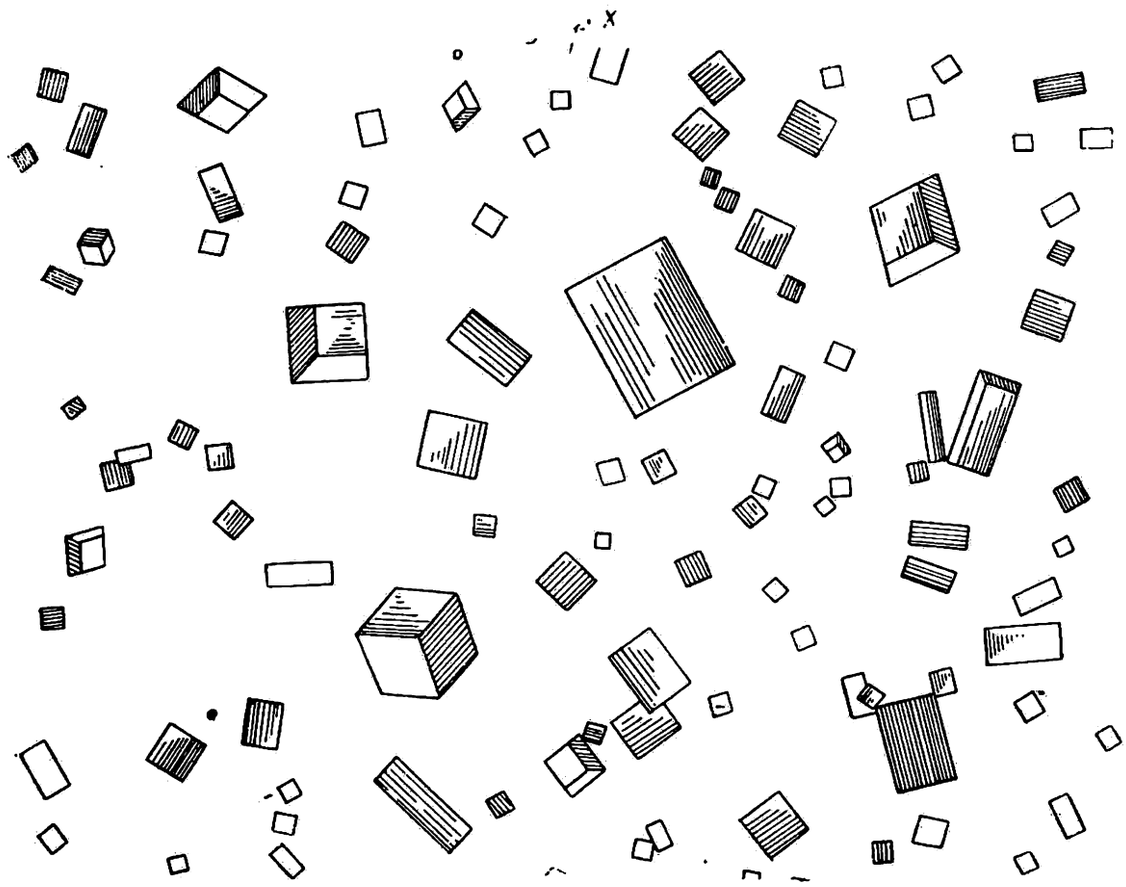


Fig. 6. Crystals of $K_2Pb[Cu(NO_2)_6]$

the slide and treat the dry residue with a drop of the special reagent for K^+ (p. 537), having the formula $Na_2Pb[Cu(NO_2)_6]$, and after one minute examine the crystals under microscope, keeping to the rules given on pp. 20-21 for microscope work. Characteristic cubic crystals of the triple nitrite $K_2Pb[Cu(NO_2)_6]$, black or brown in colour, are formed (Fig. 6). Down to 0.15 μg of K^+ can be detected by this test. The dilution limit is 1 : 6,600. The NH_4^+ ion forms similar crystals and therefore interferes with the reaction (try this).

This reagent does not give crystals with Na^+ or Mg^{++} ions.

* A gas burner can also be used for the evaporation. Keep the slide high over the flame (otherwise it will crack) or put it on the edge of the gauze.

6. **Dipicrylamine*** (Poluektov's reagent) gives an orange-red precipitate of its potassium salt with the K^+ ion. The test is most conveniently carried out by the drop method: a drop of the neutral solution to be tested for K^+ is put on a strip of filter paper and a drop of the reagent is added**. An orange-red spot is formed on the paper, unchanged when moistened with one or two drops of 2 *N* hydrochloric acid. When present in a high concentration, the NH_4^+ ion also gives a precipitate and therefore interferes with the reaction.

7. **Flame test.** Take a glass rod with a sealed-in thin platinum wire the end of which is bent into a loop (Fig. 7). First make sure that the wire is clean and does not give a colour when introduced

Fig. 7. Platinum wire and loop

into the colourless flame of a gas burner. If a colour is seen, moisten the wire with HCl solution and heat it until the colour disappears. Now touch a powdered potassium salt (preferably KCl) with the red-hot wire and put it with the adhering salt grains into the flame; note the characteristic pale violet flame. A drop of a solution of a potassium salt may be used instead of the dry salt, but the test is then less effective.

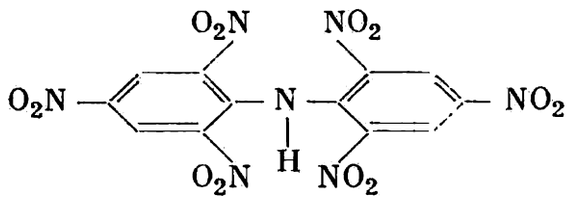
20. Reactions of the Na^+ Cation

Most sodium salts are easily soluble in water. Therefore there are very few reactions based on the formation of precipitates with the Na^+ ions. The most important are described below.

1. **Potassium dihydrogen antimonate, KH_2SbO_4** (the potassium salt of orthoantimonic acid***, H_3SbO_4), give a white crystalline precipitate of sodium dihydrogen antimonate:

$$NaCl + KH_2SbO_4 = \downarrow NaH_2SbO_4 + KCl$$

* The formula of dipicrylamine (hexanitrodiphenylamine) is



The ammonium salt can also be used. This is a dye available commercially under the name of Aurentia.

** The drop test technique is described on p. 517 et seq.

*** The reagent was formerly regarded as a salt of pyroantimonic acid, with the formula $K_2H_2Sb_2O_7$. Note that $K_2H_2Sb_2O_7 \cdot H_2O$ is identical with $2KH_2SbO_4$.

or

$$Na^+ + H_2SbO_4^- = \downarrow NaH_2SbO_4$$

Study this reaction experimentally. If the precipitate does not form immediately (owing to the formation of a supersaturated solution), rub the inside of the tube with a glass rod.

Examine the NaH_2SbO_4 precipitate. Confirm that it is crystalline.

The following conditions must be fulfilled for this reaction.

(a) *The concentration of the sodium salt must be high enough.* As the solubility of NaH_2SbO_4 is appreciable and as it tends to form supersaturated solutions, the precipitation may be delayed or may not occur at all in dilute solutions. The sensitivity of the reactions is therefore low. Accordingly, dilute solutions or solutions of unknown concentration must be first evaporated down. If no precipitate is formed, the test tube must be left to stand for some time before it is concluded that Na^+ is absent.

(b) *The solution under test must have a neutral or weakly alkaline reaction.* Acid solutions cannot be used because acids decompose the reagent to form a white amorphous precipitate of metaantimonic acid, $HSbO_3$, for example:

$$KH_2SbO_4 + HCl = H_3SbO_4 + KCl$$

$$H_3SbO_4 = \downarrow HSbO_3 + H_2O$$

or, in ionic form

$$H_2SbO_4^- + H^+ = \downarrow HSbO_3 + H_2O$$

An alkaline medium tends to dissolve the NaH_2SbO_4 precipitate to form the neutral salt, Na_3SbO_4; therefore in alkaline solution the test is even less sensitive.

A neutral solution (pH $\approx$ 7) is necessary for the test. Acid solutions are neutralized by KOH and alkaline solutions by CH_3COOH.

When this test is used for detection of Na^+, it must be borne in mind that the reagent may be decomposed by the action of carbon dioxide absorbed from the air. Amorphous precipitates of $HSbO_3$ must be distinguished from crystalline NaH_2SbO_4. *The formation of an amorphous precipitate must never be taken as an indication of the presence of* Na^+ *in the solution.*

(c) *The test must be carried out in the cold* (the test tube should preferably be cooled by immersion in a beaker with cold water), as the solubility of NaH_2SbO_4, like that of $KHC_4H_4O_6$, increases rapidly with the temperature.

2. Zinc uranyl acetate* forms a yellowish crystalline precipitate of zinc sodium uranyl acetate, having the formula

---

* The uranyl group is the bivalent UO_2^{++} group which acts as a metal in uranium salts.

$(CH_3COO)_2Zn \cdot CH_3COONa \cdot 3(CH_3COO)_2UO_2 \cdot 9H_2O$, with sodium salts in neutral or acetic acid solutions.

To carry out the test, add not more than two or three drops of a neutral solution of a sodium salt to about 0.5 ml of the reagent solution and rub the inside of the test tube with a glass rod. Examine the precipitate.

This reaction is much more sensitive than the test with potassium dihydrogen antimonate.

Moreover, this reaction is specific for sodium. The presence of 20-fold amounts of K^+, NH_4^+, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Al^{+++}, Fe^{+++}, Cr^{+++}, Mn^{++}, Zn^{++}, Co^{++}, Ni^{++}, Cd^{++}, Bi^{+++}, Cu^{++}, Pb^{++} and Hg^{++} does not interfere with detection of sodium. Therefore zinc uranyl acetate is used for detecting Na^+ in salts of zinc, manganese, iron, lead, copper, etc. In the presence of large amounts of K^+ needle-shaped crystals of $CH_3COOK \cdot (CH_3COO)_2UO_2$ may be formed. Therefore if the unknown solution contains a high concentration of K^+ (if an abundant precipitate is formed in the test for K^+), the solution should be diluted to two or three times the original volume with water before the tests with zinc uranyl acetate, a few drops of the diluted solution being taken for the test for Na^+.

The solution used for detection of Na^+ should be as nearly neutral as possible. Acid solutions are previously neutralized by ammonia or zinc oxide. In the latter case excess zinc oxide is filtered off and the filtrate is tested for Na^+.

A precipitate of $CH_3COONa \cdot (CH_3COO)_2Mg \cdot 3(CH_3COO)_2UO_2 \cdot 9H_2O$, analogous to that described above, is formed if the reagent used is the magnesium instead of the zinc salt.

3. Microcrystalloscopic test. Put a drop of the sodium salt solution on a glass slide and carefully evaporate it to dryness. Cool the residue, treat it with a drop of uranyl acetate solution $(CH_3COO)_2UO_2$, and after a few minutes examine the crystals of sodium uranyl acetate, $CH_3COONa \cdot (CH_3COO)_2UO_2$, under the microscope. They are regular tetrahedra or octahedra (Fig. 8).

The test is very sensitive (detectable minimum 0.8 μg Na^+). In the presence of Mg^{++} yellow crystals of the triple salt $CH_3COONa \cdot (CH_3COO)_2Mg \cdot 3(CH_3COO)_2UO_2 \cdot 9H_2O$ are formed, similar to the crystals formed with sodium.

4. Flame test. Volatile sodium salts colour the flame bright yellow. This is a very characteristic test for sodium.

Study it experimentally in the same manner as the flame test for potassium.

Now mix solutions of potassium and sodium salts, dip a platinum wire into the mixture, and repeat the flame test. The violet colour characteristic of potassium cannot be seen. To detect it, the flame is viewed through blue glass or through a solution of indigo placed in

a special "indigo prism" (Fig. 9); the blue glass or indigo solution absorbs the yellow sodium light. Confirm this by experiment.

It must be remembered that the flame test for sodium is highly sensitive (the detectable minimum is 0.0001 μg) and that sodium compounds occur everywhere; for example, they are present in dust.

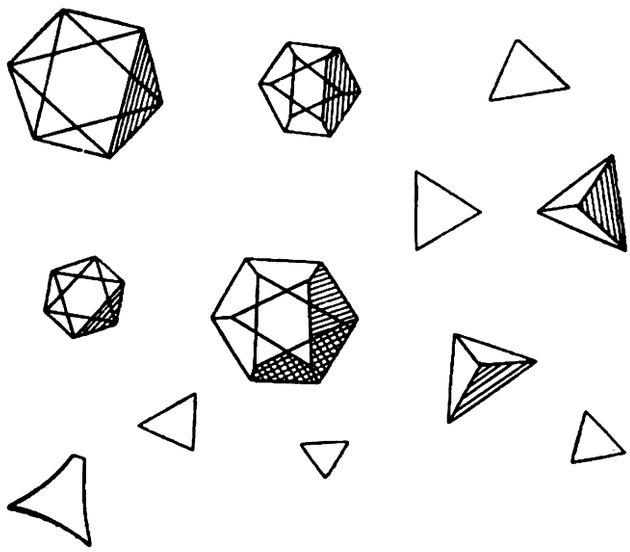


Fig. 8. Crystals of $CH_3COONa \cdot (CH_3COO)_2UO_2$

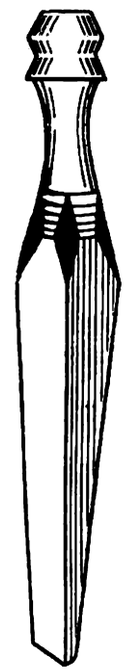


Fig. 9. Indigo prism

are extracted by water from glassware, etc. Therefore *only a bright yellow flame colouration which persists for several seconds* may be taken as evidence of the presence of measurable amounts of sodium in a given substance.

21. Reactions of the NH_4^+ Cation

The most important reactions for the ammonium ion are described below.

1. Caustic alkalies, NaOH and KOH, liberate ammonia gas from solutions of ammonium salts on heating:

$$NH_4Cl + NaOH = NH_3\uparrow + NaCl + H_2O$$

Study this reaction experimentally. Add caustic alkali to a solution of an ammonium salt, such as NH_4Cl or $(NH_4)_2SO_4$, and heat. Note the odour of the gas evolved. Ammonia may be detected in other ways apart from its smell.

(a) Moisten a piece of red litmus paper with water and bring it up to the mouth of the test tube (without touching it). The paper turns

blue because NH_3 dissolves in water to give an alkali (NH_4OH).

(b) Phenolphthalein paper may be used instead of litmus. It is turned red by ammonia and the colour change is more distinct.

(c) Repeat the experiment with a piece of filter paper moistened with $Hg_2(NO_3)_2$ solution instead of phenolphthalein paper. The paper is turned black by the action of NH_3.

This reaction is represented by the equation*

$$2Hg_2(NO_3)_2 + 4NH_3 + H_2O = \left[O\begin{matrix}Hg\\ \diagup\diagdown \\ Hg\end{matrix}NH_2 \right] NO_3 + \downarrow 2Hg + 3NH_4NO_3$$

or in ionic form

$$2Hg_2^{++} + 4NH_3 + H_2O = \left[O\begin{matrix}Hg\\ \diagup\diagdown \\ Hg\end{matrix}NH_2 \right] NO_3 + \downarrow 2Hg + 3NH_4^+$$

(d) Bring a glass rod moistened with concentrated HCl up to the mouth of the test tube in which ammonia is evolved. A white "smoke" forms owing to the formation of minute NH_4Cl crystals:

$$NH_3 + HCl = NH_4Cl$$

2. Nessler's reagent, which is a mixture of the complex salt $K_2[HgI_4]$ with KOH, gives a characteristic red-brown precipitate of the composition $\left[O\begin{matrix}Hg\\ \diagup\diagdown \\ Hg\end{matrix}NH_2 \right] I$ with solutions of ammonium salts:

$$NH_4Cl + 2K_2[HgI_4] + 4KOH = \downarrow \left[O\begin{matrix}Hg\\ \diagup\diagdown \\ Hg\end{matrix}NH_2 \right] I + KCl + 7KI + 3H_2O$$

Very small amounts ("traces") of ammonium salts give a yellow colour instead of the red-brown precipitate. This reaction is extremely sensitive.

To study this test, take not more than one or two drops of NH_4Cl solution, add water to half-fill the test tube, and then add a small amount of Nessler's reagent (it should be taken in excess over the amount of ammonium salt present, as the precipitate dissolves in excess ammonium salt).

---

* The formula of the resultant mercury compound is easy to remember if it is noticed that the compound is formed by replacement of two hydrogen atoms in the NH_4^+ ion by the bivalent $O\begin{matrix}Hg-\\ \diagup \\ \diagdown \\ Hg-\end{matrix}$ group.

Nessler's reagent contains alkali; alkalies precipitate insoluble hydroxides, many of which are coloured, with most cations. These coloured precipitates may obscure the colour of the precipitate formed in the presence of the NH_4^+ ion. Therefore this reaction is less specific for NH_4^+ than the caustic alkali test. However, this difficulty is easily avoided by carrying out the experiment in an apparatus known as a *gas chamber* (Fig. 10). It consists of two watch-glasses.

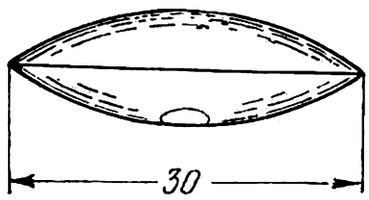


Fig. 10. Gas chamber

A drop of a mixture of an ammonium salt solution and an alkali is placed on one of the glasses. A drop of Nessler's reagent is put on the other glass and the first is then covered with it. The NH_3 evolved by the action of the alkali is absorbed by the drop of reagent and the characteristic red-brown precipitate is formed.

An alternative method is to precipitate the metal hydroxides in a test tube (by adding excess NaOH or KOH), filter off the precipitate, and add Nessler's reagent to the filtrate.

3. Effects of reagents for K^+ and Na^+ ions on the NH_4^+ ion. Having studied the most important qualitative reactions of the NH_4^+ ion, we must also find how it behaves with reagents used for detection of K^+ and Na^+, as this is necessary for understanding the systematic procedure for analysis of Group I cations.

(a) $NaHC_4H_4O_6$ and $Na_3[Co(NO_2)_6]$ form precipitates of ammonium salts with NH_4^+, indistinguishable in appearance from those given by K^+ ions. Confirm this experimentally*. *It follows that* NH_4^+ *interferes with detection of* K^+.

(b) Solutions of ammonium salts may give a white amorphous precipitate of $HSbO_3$ with KH_2SbO_4, because they have an acid reaction due to hydrolysis:

$$NH_4Cl + H_2O \rightleftarrows NH_4OH + HCl \text{ (hydrolysis)}$$

$$HCl + KH_2SbO_4 = H_3SbO_4 + KCl$$

$$H_3SbO_4 = \downarrow HSbO_3 + H_2O$$

Therefore NH_4^+ interferes with the detection of Na^+ by this reaction.

* A fairly concentrated (e.g., saturated) solution of NH_4Cl should be taken for the reaction with $NaHC_4H_4O_6$.

However, Na^+ can be detected in the presence of NH_4^+ by the reaction with zinc uranyl acetate or by the microcrystalloscopic test with $UO_2(CH_3COO)_2$.

4. Separation of the ammonium ion. We have just seen that NH_4^+ interferes with detection of K^+ and (in the reaction with KH_2SbO_4) of Na^+.

Therefore: (a) the solution must be tested for NH_4^+ before the tests for K^+ and Na^+; (b) if NH_4^+ is found, it must be completely removed from the mixture of the Group I cations*.

The removal of the ammonium ion is based on the volatility of ammonium salts on heating. The solution from which NH_4^+ ions are to be removed is evaporated to dryness in a porcelain basin and the dry residue is heated strongly until no more white "smoke" is evolved. In the presence of NH_4Cl the reaction proceeds according to the equation:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

The equation shows that the reaction is reversible. At high temperatures NH_4Cl decomposes with formation of gaseous NH_3 and HCl, which volatilize from the basin. However, after leaving the high temperature zone these substances recombine to form NH_4Cl. The white "smoke" formed when ammonium chloride is heated consists of small crystals of this salt.

Potassium and sodium salts are much less volatile than ammonium salts. It is found experimentally that KCl and NaCl do not lose appreciably in weight when heated for half an hour at 800°. However, at 1,000° these salts are volatilized almost completely (if small portions are taken). It follows that excessive and prolonged heating should be avoided in the removal of NH_4^+. The residue after the heating is dissolved in water; the solution contains all the original cations with the exception of NH_4^+.

If the ammonium salt is derived not from HCl but from a non-volatile acid such as H_3PO_4, only ammonia is volatilized on heating while the acid remains in the basin. Obviously no white "smoke" is formed in this case. Neither is it formed from NH_4NO_3 or salts of acids which are strong oxidizing agents. These decompose in a different manner; for example, the decomposition of NH_4NO_3 is represented by the equation**

$$NH_4NO_3 = 2H_2O + N_2O\uparrow$$

* However, there is a method for analysis of Group I in which the ammonium ion is bound by the action of formaldehyde and not removed (see pp. 98-99).

** NH_4NO_3 decomposes with formation of N_2O when ammonium nitrate is heated cautiously at 260-280°; in general, NH_4NO_3 may decompose in accordance with seven different equations, dependent on the conditions.

However, whatever ammonium salt is taken, when it is heated it always either volatilizes or decomposes with formation of gaseous products, and the object—removal of NH_4^+ ions—is achieved in one way or another.

As already stated, to remove ammonium salts the solution must be evaporated in a porcelain basin, never in glass, because the latter

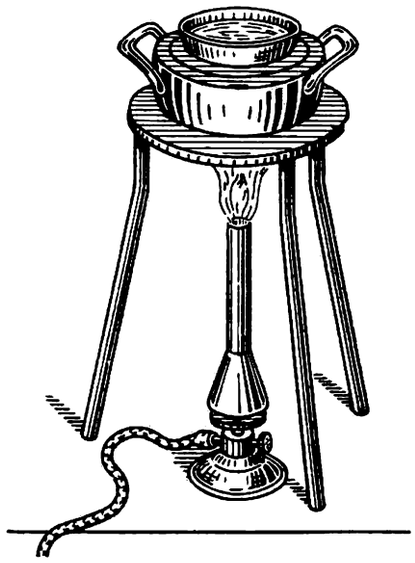


Fig. 11. Evaporation on a water bath

often cracks during the operation. The basin is put on a gauze on a tripod or the ring of a stand and heated cautiously to avoid splashing. Splashing becomes most pronounced near the end of the evaporation. To avoid this, it is best to complete the evaporation on a water bath, which is a metal vessel filled with boiling water (Fig. 11).

At the end of the evaporation the dry residue is heated until fuming ceases completely. *This operation must always be carried out in a fume cupboard.* Towards the end of the heating the dry residue is scraped by means of a glass rod from the sides of the basin to the bottom and heated thoroughly again. As in every other separation, complete removal of the ammonium salt must be confirmed. A small portion of the dry residue is transferred to a test tube, dissolved in water, and tested with Nessler's reagent.

When the ammonium salts have been removed completely the basin is allowed to cool and a *small amount* of water is added (otherwise the subsequent tests for K^+ and Na^+ will not work well). The liquid should be filtered because the solution often contains small amounts of organic impurities which char on heating.

Instead of removing the ammonium ion before detection of K^+ it may be converted into undissociated molecules of the organic compound hexamethylene-

tetramine (or urotropin), $(CH_2)_6N_4$, by addition of a solution of formaldehyde, CH_2O. The reaction is represented by the equation

$$4NH_4^+ + 6CH_2O \rightleftarrows (CH_2)_6N_4 + 6H_2O + 4H^+$$

and goes to completion only if the hydrogen ions formed are removed. This can be effected by means of sodium carbonate solution, which also precipitates cations of all the other groups and Mg^{++} as the corresponding carbonates (or hydroxides).

This method can be used for fractional detection of potassium. If the solution contains ammonium ions, to 1-2 ml of the solution an equal volume of 40% formaldehyde solution (formalin) and a drop of phenolphthalein indicator are added. Sodium carbonate solution is then added drop by drop until a permanent red colour appears, indicating an excess of Na_2CO_3. If a precipitate is formed the solution is heated for 1-2 minutes, the liquid is filtered, and the precipitate is rejected. The filtrate is acidified by 2 *N* CH_3COOH solution until the red colour disappears and tested for K^+ with $Na_3[Co(NO_2)_6]$.

22. Reactions of the Mg^{++} Cation

As already stated, the reactions of the Mg^{++} cation differ considerably from those of the other Group I cations. The following are the most characteristic.

1. Caustic alkalies (OH^- ions) give a white amorphous precipitate of $Mg(OH)_2$ with Mg^{++}:

$$MgCl_2 + 2KOH = \downarrow Mg(OH)_2 + 2KCl$$

or

$$Mg^{++} + 2OH^- = \downarrow Mg(OH)_2$$

Since the hydroxides of the other Group I cations are easily soluble in water, this reaction can be used for separation of Mg^{++}.

Magnesium hydroxide is soluble in acids and in ammonium salts. Confirm this experimentally. Therefore Mg^{++} *cannot be completely separated in presence of* NH_4^+ *ions.* At high concentrations of ammonium salts $Mg(OH)_2$ may not be precipitated at all, despite the presence of Mg^{++} in the solution. Confirm this by means of the following experiments.

(a) To 1-2 ml of a solution of a magnesium salt add 1-2 ml each of water and 2 *N* NH_4OH solution. What happens?

(b) Repeat this experiment with saturated NH_4Cl solution instead of water. Does a precipitate form?

It was shown in Sec. 12 that NH_4Cl strongly suppresses the dissociation of NH_4OH and thus lowers the OH^- ion concentration. That is why $Mg(OH)_2$ is not precipitated in the presence of NH_4Cl. This point will be discussed more fully in Sec. 26. In analytical practice ammonium salts are often used to prevent precipitation of $Mg(OH)_2$.

2. Disodium hydrogen phosphate, Na_2HPO_4, in the presence of NH_4OH and NH_4Cl forms a white crystalline precipitate of magnesium ammonium phosphate, $MgNH_4PO_4$, with magnesium salts:

$$MgSO_4 + Na_2HPO_4 = MgHPO_4 + Na_2SO_4$$
$$MgHPO_4 + NH_4OH = MgNH_4PO_4 + H_2O$$

Adding the two equations, we have

$$MgSO_4 + Na_2HPO_4 + NH_4OH = \downarrow MgNH_4PO_4 + Na_2SO_4 + H_2O$$

or

$$Mg^{++} + HPO_4^{--} + NH_4OH = \downarrow MgNH_4PO_4 + H_2O$$

The ammonium salt is added to prevent precipitation of $Mg(OH)_2$ by the action of ammonia (see above).

This most important qualitative test for Mg^{++} is carried out as follows.

To a small amount of a magnesium salt solution add enough NH_4Cl solution to prevent precipitation of $Mg(OH)_2$ on subsequent addition of NH_4OH. Now add dilute Na_2HPO_4 solution drop by drop, shaking the contents of the test tube after each addition. Examine the small crystals of $MgNH_4PO_4$ suspended in the liquid and adhering to the walls. Confirm that the precipitate is soluble in acids.

If a crystalline precipitate is not obtained immediately by this method, the amorphous precipitate (or suspension) which forms may be dissolved in a few drops of an acid, and then reprecipitated by dropwise addition of ammonia*.

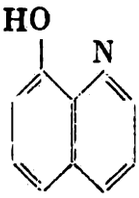
Ammonia must be added until the smell is quite distinct, or until the liquid is slightly alkaline to phenolphthalein (pink colour with phenolphthalein paper, corresponding to pH $\approx$ 9). A strongly alkaline reaction should be avoided, as at pH $>$ 10 a non-characteristic precipitate of $Mg_3(PO_4)_2$ is formed instead of $MgNH_4PO_4$. Precipitation is delayed in dilute solutions. It is accelerated if the walls of the test tube are rubbed with a glass rod. In the absence of a precipitate the liquid must be left to stand before it can be assumed that Mg^{++} is absent.

3. 8-Hydroxyquinoline, HC_9H_6NO,** forms a yellowish-green precipitate of the magnesium compound $Mg(C_9H_6NO)_2$ with ammoniacal

---

* In the absence of NH_4OH the Mg^{++} ion gives a non-characteristic amorphous precipitate of $MgHPO_4$ with Na_2HPO_4.

** The structural formula of 8-hydroxyquinoline is



solutions of magnesium salts. To carry out the test add NH_4Cl and NH_4OH to 1-2 ml of a solution of a magnesium salt, followed by a 5% alcoholic solution of the reagent. Neither Na^+, K^+, NH_4^+ nor Ba^{++}, Sr^{++} and Ca^{++} interfere with the reaction.

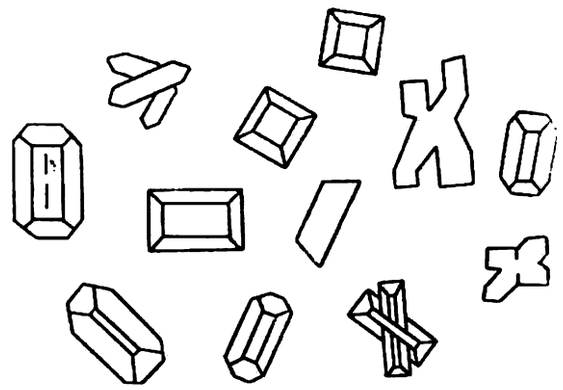


Fig. 12. Crystals of $MgNH_4PO_4 \cdot 6H_2O$ formed by slow crystallization

4. Microcrystalloscopic test. The Mg^{++} ion can also be detected by the reaction of $MgNH_4PO_4$ formation discussed above. Figure 12 shows the crystals of this salt formed by slow crystallization from dilute solutions. If the crystallization is rapid (Fig. 13), more concentrated solutions or solutions containing large amounts of ammonium salts give star-shaped or tree-like (dendritic) crystals.

Put a drop of a magnesium salt solution containing a small amount of NH_4Cl on a glass slide. Then hold the slide, with the drop on the underside, over the neck of a flask containing 25% NH_4OH for

Fig. 13. Crystals of $MgNH_4PO_4 \cdot 6H_2O$ formed by rapid crystallization

a few minutes. Now introduce a small crystal of $Na_2HPO_4 \cdot 12H_2O$ into the drop and examine the crystals formed under the microscope.

The detectable minimum is 0.012 μg Mg^{++}; the dilution limit is 1 : 83,000. Potassium, sodium and ammonium salts do not interfere.

5. Colour test. Magnesium hydroxide adsorbs certain organic dyes, the adsorbed dye differing in colour from the same dye in

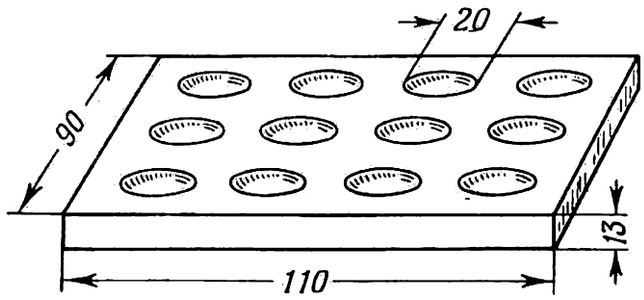


Fig. 14. Spot plale

solution. This can be used for detection of Mg^{++}. A suitable reagent is *p*-nitrobenzene-azo-resorcinol*. This dye is red or red-violet in alkaline solution, but when adsorbed by magnesium hydroxide it colours the latter a deep blue.

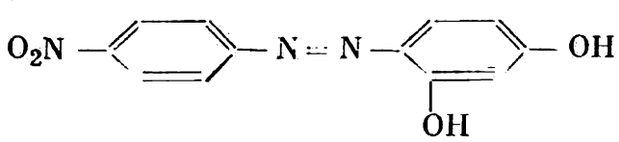
The test is conveniently carried out on a *spot plate*, which is a porcelain tile with shallow depressions (Fig. 14). Put a drop of a magnesium salt solution in one of the depressions and add one or two drops of an alkaline solution of the reagent. Dependent on the amount of Mg^{++}, either a blue precipitate is formed or the red-violet colour of the reagent changes to blue; this colour change is very distinct against the white porcelain.

A yellow colour indicates that the solution tested is too acid. A few drops of alkali must then be added to it. Large amounts of ammonium salts should be previously removed. Neither Ca^{++}, Sr^{++} and Ba^{++} nor Al^{+++} and Mn^{++} interfere**. The detectable minimum is 0.5 μg Mg^{++}.

6. N. A. Tananaev's drop reaction. This is based on the partial solubility of magnesium hydroxide in water to give pH ≈ 10, at which phenolphthalein is bright red.

---

* Its structural formula is



** Coloured compounds are also formed by *p*-nitrobenzene-azo-resorcinol with the hydroxides of nickel, cobalt, and cadmium.

Put a drop of the unknown solution and a drop of 2 *N* ammonia solution on a strip of phenolphthalein paper. The paper turns red, which is due both to the presence of excess NH_4ON and to the formation of magnesium hydroxide by the reaction

$$Mg^{++} + 2NH_4OH = \downarrow Mg(OH)_2 + 2NH_4^+$$

Now carefully dry the paper over a flame. Ammonia and water are volatilized and the red colour disappears. In the presence of Mg^{++} a drop of water turns the paper red again owing to partial dissolution of $Mg(OH)_2$; in the absence of Mg^{++} it remains colourless.

With this test Mg^{++} can be detected in the presence of K^+, Na^+, Ca^{++}, Sr^{++} and Ba^{++}. Cations of Groups III, IV and V must be previously removed. The presence of NH_4^+ ions prevents precipitation of $Mg(OH)_2$, and they must also be absent.

7. Effects of reagents for K^+ and Na^+ on the Mg^{++} cation. Having examined the most important reactions of the Mg^{++} ion, let us consider its behaviour with the reagents used for detection of K^+ and Na^+.

(a) $NaHC_4H_4O_6$ and $Na_3[Co(NO_2)_6]$ do not form precipitates with Mg^{++}. *Therefore* Mg^{++} *does not interfere with the detection of* K.

(b) KH_2SbO_4 forms a white crystalline precipitate of $Mg(H_2SbO_4)_2$ with Mg^{++}, indistinguishable in appearance from NaH_2SbO_4 (try this). Therefore Mg^{++} must be removed before detection of Na^+ by the reaction with KH_2SbO_4. It is preferable in such cases to use the reaction with zinc uranyl acetate or the microcrystalloscopic test for Na^+, as the Mg^{++} ion does not interfere with these tests.

8. Soluble carbonates (CO_3^{--} ions) form a white amorphous precipitate of basic magnesium carbonate, $(MgOH)_2CO_3$, with Mg^{++}; unlike Na_2CO_3, K_2CO_3 and $(NH_4)_2CO_3$, this is sparingly soluble in water:

$$2MgSO_4 + 2Na_2CO_3 + H_2O = \downarrow (MgOH)_2CO_3 + 2Na_2SO_4 + CO_2 \uparrow$$

or

$$2Mg^{++} + 2CO_3^{--} + H_2O = \downarrow (MgOH)_2CO_3 + CO_2 \uparrow$$

The precipitate is soluble in acids and in ammonium salts (try). It follows that if $(NH_4)_2CO_3$ is used as the reagent instead of Na_2CO_3, the precipitation of Mg^{++} cannot be complete, as precipitation is accompanied by dissolution of the precipitate:

$$2MgCl_2 + 2(NH_4)_2CO_3 + H_2O \rightleftarrows \downarrow (MgOH)_2CO_3 + 4NH_4Cl + CO_2 \uparrow$$

If an ammonium salt is added to the solution to increase the ammonium salt concentration, $(MgOH)_2CO_3$ is not precipitated at all. Test this experimentally.

We know that $(NH_4)_2CO_3$ is the group reagent for Group II cations, precipitating them as insoluble carbonates. It can be seen that Mg^{++}

cannot be precipitated completely with Group II. To ensure that it remains completely in solution with Group I, it is preferable to precipitate Group II cations by ammonium carbonate in the presence of NH_4Cl.

It has already been pointed out that the behaviour of Mg^{++} with ammonium carbonate in the presence of NH_4Cl justifies its inclusion in cation Group I.

23. Analysis of Mixtures of Group I Cations

Having studied the reactions of Group I cations, let us compare their behaviour with the most important reagents (Table 9). Heavy type in the table indicates the most characteristic reactions or properties of the cations, used for their detection or separation. A dash indicates the absence of a precipitate (or colour).

The table clearly demonstrates the conclusions reached in our study of the reactions of Group I cations: (a) the NH_4^+ ion interferes with detection of K^+ and Na^+ (by the reaction with KH_2SbO_4); (b) other Group I cations do not interfere with detection of NH_4^+ and Mg^{++}; (c) K^+ can also be detected in the presence of Na^+ and Mg^{++}; (d) NH_4^+ can be removed by evaporation of the solution followed by strong heating of the residue, while Mg^{++} can be removed by precipitation as $Mg(OH)_2$ by the action of alkali. The analytical procedure for mixtures of Group I cations, based on the reactions studied, is described in detail below.

In starting analysis it is important to remember that the aim of analysis is not only to detect the ions (or elements) present in a given substance but also *to determine which are the main components and which are present as impurities.* In the case of wet-way tests it is easy to decide this from the amount of precipitate formed. On the other hand, no such conclusions can be drawn from flame tests; yet it is usually very important to settle this question in order to choose the most suitable methods for quantitative analysis of the substance.

Therefore, although Na^+ and K^+ could be detected by the fractional method with the aid of flame tests in analysis of Group I cations. such tests alone cannot suffice.

It is essential to find Na^+ and K^+ in the wet way, using flame tests merely for confirmation. Moreover, too much reliance should not be placed on the flame test because in certain cases (for example. in the detection of Na^+) it can easily lead to error because of its extreme sensitivity.

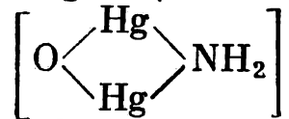
Before the detection of individual ions it is necessary to estimate the pH of the unknown solution, since a suitable pH is one of the most important conditions for analytical reactions. Moreover, such

estimation gives some indication of the composition of the solution. For example, a weakly acid reaction suggests the possible presence of NH_4^+ or Mg^{++}. A strongly acid reaction (pH = 2) indicates the presence of acid salts (such as $NaHSO_4$) or free acids, while strong alkalinity shows the presence either of free alkali or of potassium or sodium salts of weak acids (K_2CO_3 or Na_2CO_3). The result of the pH determination must be recorded together with the relevant conclusions in the analytical report and presented to the instructor together with the remaining results.

ANALYSIS OF A MIXTURE OF GROUP I CATIONS

1. Determination of the solution pH with the aid of a range of indicators or with the universal indicator (see Sec. 17).

2. Detection of ammonium. The analysis should be started with the detection of ammonium, the presence of which interferes with detection of K^+ and Na^+. These ions, on the other hand, do not interfere with detection of NH_4^+, because under the conditions of analysis ammonia can be formed only from an ammonium salt on heating with an alkali.

To detect NH_4^+, add an excess (3-5 ml) of NaOH or KOH solution to a separate portion (1-2 ml)* of the unknown solution and heat to boiling. Stop the heating, cautiously smell the gas evolved from the test tube and test it with red litmus paper moistened with water (*without touching the walls of the tube, which are wet with alkali*). Another portion of the unknown solution may be tested with Nessler's reagent (see Sec. 21-2). The formation of a red-brown precipitate of  I confirms** the presence of NH_4^-.

3. Detection of magnesium. Magnesium may also be detected by the fractional method, as the other Group I cations do not interfere.

To a separate portion of the solution add NH_4OH (until the liquid smells of ammonia), NH_4Cl, and then Na_2HPO_4 drop by drop. If no precipitate forms, leave it to stand.

A white crystalline precipitate of $MgNH_4PO_4$ indicates the presence of Mg^{++}.

Alternatively, a drop of the solution can be tested for Mg^{++} microcrystalloscopically as described in Sec. 22-4, or magnesium can be

---

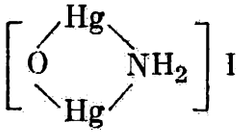
* Except where otherwise stated, the volumes of reagents given here and elsewhere in the book subsequently are approximate.

** As Nessler's reagent contains alkali in addition to $K_2[HgI_4]$, it gives a white precipitate of $Mg(OH)_2$ with magnesium salts.

Table 9

Reactions of Group I Cations

Reagents	Cations			
	K^+	Na^+	NH_4^+	Mg^{++}
$NaHC_4H_4O_6$	White crystalline precipitate **$KHC_4H_4O_6$**	—	White crystalline precipitate $NH_4HC_4H_4O_6$	—
$Na_3[Co(NO_2)_6]$	Yellow crystalline precipitate **$K_2Na[Co(NO_2)_6]$**	—	Yellow crystalline precipitate $(NH_4)_2Na[Co(NO_2)_6]$	—
KH_2SbO_4	—	White crystalline precipitate **NaH_2SbO_4**	White amorphous precipitate $HSbO_3$	White crystalline precipitate $Mg(H_2SbO_4)_2$
CH_3COOH + + $(CH_3COO)_2Zn$ + + $(CH_3COO)_2UO_2$	—*	Yellowish crystalline precipitate **$CH_3COONa \cdot (CH_3COO)_2Zn \cdot 3(CH_3COO)_2UO_2 \cdot 9H_2O$**	—	—
KOH, NaOH	—	—	**NH_3** evolved	White amorphous precipitate **$Mg(OH)_2$**

Nessler's reagent $K_2[HgI_4]+KOH$	—	—	Red-brown precipitate 	White amorphous precipitate $Mg(OH)_2$
$Na_2HPO_4+NH_4OH$ in presence of NH_4Cl	—	—	—	White crystalline precipitate $MgNH_4PO_4$
8-Hydroxyquinoline	—	—	—	Greenish yellow precipitate $Mg(C_9H_6NO)_2$
p-Nitrobenzene-azo-resorcinol	—	—	—	Dark blue precipitate or colour
$(NH_4)_2CO_3+NH_4Cl$	—	—	—	No precipitate
Action of heat on salts	Not volatile	Not volatile	Volatile	Not volatile
Flame colouration	Violet	Yellow	—	—

* At high K^+ concentrations $CH_3COOK \cdot (CH_3COO)_2UO_2$ may be precipitated.

detected by the reactions with *p*-nitrobenzene-azo-resorcinol (Sec. 22-5) or with 8-hydroxyquinoline (Sec. 22-3).

4. Removal of ammonium. If the NH_4^+ ion is present*, it must be removed before detection of K^+. Transfer all the solution to a porcelain basin, evaporate to dryness, and heat strongly until no more white fumes are evolved. Dissolve a few grains of the dry residue in water and test with Nessler's reagent. When the complete removal of NH_4^+ has been confirmed, leave a small portion of the dry residue for the flame test (see below, 7) and dissolve the rest in a small volume (2-3 ml) of hot water (if too much water is used the solution may be too dilute and the tests for K^+ and Na^+ might therefore fail).

Magnesium salts undergo hydrolysis during evaporation to give a white basic salt, MgOHCl, which is sparingly soluble in water; therefore if the residue does not dissolve completely in water, the liquid must be filtered and the insoluble residue rejected. Test the filtrate for K^+ and Na^+ as described below.

5. Detection of potassium. Test the resultant solution with litmus paper**. Test a separate portion for K^+ with $Na_3[Co(NO_2)_6]$; if a precipitate is not formed immediately, allow the solution to stand. A yellow precipitate of $K_2Na[Co(NO_2)_6]$ indicates the presence of K^+.

Alternatively, evaporate a drop of the solution to dryness on a glass slide, cool, add a drop of the reagent for K^+ used for the microcrystalloscopic test (see Sec. 19-5), and after 1-2 minutes examine the precipitate under the microscope. The formation of black cubic crystals of the complex salt $K_2Pb[Cu(NO_2)_6]$ confirms the presence of potassium.***

6. Detection of sodium. Take about 0.5 ml of zinc uranyl acetate solution and add 2-3 drops (not more) of the neutral unknown solution; rub the walls of the test tube with a glass rod. A yellowish crystalline precipitate of zinc sodium uranyl acetate indicates the presence of Na^+.

If much K^+ is present in solution, a white crystalline precipitate of $CH_3COOK \cdot (CH_3COO)_2UO_2$ may form. Therefore in the presence of K^+ the solution must be diluted with an equal volume of distilled water; after thorough

---

* In the absence of NH_4^+ this operation is superfluous, and K^+ and Na^+ may be detected immediately. Remember that in systematic analysis NH_4^+ is introduced when $(NH_4)_2CO_3$ is added to precipitate Group II cations. Instead of removing NH_4^+ we can convert it into undissociated $(CH_2)_6N_4$ molecules (see pp. 98-99).

** To test the solution, transfer a drop to a strip of blue (or red) litmus paper by means of a glass rod. If the solution is acid, a small amount of CH_3COONa must be added in the $Na_3[Co(NO_2)_6]$ test for K^+.

*** Remember that NH_4^+ also gives these two reactions; if it is not removed, K^+ may be detected in error.

mixing the diluted solution is tested. The precipitated double salt $CH_3COOK \cdot (CH_3COO)_2UO_2$ is easily distinguished from the precipitate given by Na^+ if the turbid liquid is examined under the microscope. The Na^+ precipitate consists of octahedral or tetrahedral crystals (Fig. 8), whereas the $CH_3COOK \cdot (CH_3COO)_2UO_2$ crystals are needle-shaped.

Alternatively, evaporate a drop of the solution to dryness on a glass slide, cool, add a drop of zinc uranyl acetate solution to the residue, and after 1-2 minutes examine under the microscope.

Formation of $CH_3COONa \cdot (CH_3COO)_2UO_2$ crystals (see Fig. 8) confirms the presence of Na^+.

Note. In the absence of Mg^{++} the reaction with KH_2SbO_4 (Sec. 20-1) may be used for detection of Na^+. The formation of a *crystalline precipitate* of NaH_2SbO_4 indicates the presence of Na^+. In the presence of Mg^{++} this test can be used only after removal of magnesium, as Mg^{++} gives with KH_2SbO_4 a white crystalline precipitate of $Mg(H_2SbO_4)_2$, indistinguishable in appearance from NaH_2SbO_4. To separate Mg^{++} transfer the solution to a porcelain basin, *add* KOH *solution until strongly alkaline* (this is permissible because K^+ has already been tested for), boil, and filter off the precipitated $Mg(OH)_2$. Before the test for sodium the alkaline filtrate must be neutralized with HCl. The preferable procedure is as follows. First add HCl until acid, evaporate the solution to dryness in a porcelain basin, and calcine the residue slightly to remove excess HCl. When cool, dissolve the calcined residue (KCl and NaCl) in 1-2 ml of water. filter if necessary, and test for Na^+ with KH_2SbO_4.

7. **Confirmatory test for K^+ and Na^+.** It is useful to confirm the presence of K^+ and Na^+ by the flame test, viewing the flame with the naked eye (test for Na^+) and through indigo solution or blue glass (test for K^+).

Detection of potassium and sodium by the fractional method. If the unknown solution contains cations of Groups II-V, they are progressively precipitated. Group I cations are detected in the solution remaining after their removal. Separation reactions always involve loss of part of the ions which should remain in solution but are partially entrained with the precipitate owing to surface adsorption and other causes (see Sec. 41). Therefore the concentrations of Group I cations in solution are very much reduced by the time the stage of their analysis is reached. Moreover, since the tests for K^+ and Na^+ are of relatively low sensitivity, it is obvious that these ions may sometimes be "lost" in systematic analysis. As a safeguard against such error, if K^+ and Na^+ are not found in systematic analysis they should be tested for by the fractional method, i.e., directly in separate portions of the original solution, as follows.

(a) *Detection of potassium ion.* If ammonium is present*, to 1-2 ml of the solution add an equal volume of 40% formaldehyde solution (formalin), CH_2O, which converts NH_4^+ ions to undissociated molecules of urotropin, $(CH_2)_6N_4$ (see p. 99). Then add a drop of phenolphthalein, and a solution of *chemically pure* Na_2CO_3 drop by drop until the colour changes to red. This neutralizes the acid formed in the reaction between NH_4^+ and formaldehyde, and precipitates the cations of the other groups together with Mg^{++}. Filter off and reject the precip-

* In the absence of ammonium it is unnecessary to add formaldehyde. In such cases chemically pure Na_2CO_3 is added immediately to the solution in the presence of phenolphthalein, etc. It is also possible to remove NH_4^+, by evaporation and heating, from the filtrate remaining after precipitation with Na_2CO_3.

itate (carbonates, basic carbonates, and hydroxides). Acidify the filtrate with 2 *N* acetic acid until the red colour disappears and test for K^+ with $Na_3[Co(NO_2)_6]$.

(b) *Detection of sodium.* To another portion of the solution add *chemically pure* K_2CO_3 solution; make sure that the precipitation is complete, filter and reject the precipitate. Acidify the filtrate slightly with 2 *N* acetic acid (test with litmus). Add 2-3 drops of this solution to about 0.5 ml of zinc uranyl acetate solution. Precipitation of crystals seen to be octahedral under the microscope (see Fig. 8) indicates the presence of Na^+. In the absence of sodium, needle-shaped crystals of $CH_3COOK \cdot (CH_3COO)_2UO_2$ may be formed.

Chemically pure Na_2CO_3 *and* K_2CO_3, *free from potassium and sodium impurities respectively, must be used in the above tests.*

QUESTIONS AND PROBLEMS

1. Can all Group I cations be precipitated by any single reagent?
2. What are the conditions which must be satisfied in detection of K^+ by the reaction with $NaHC_4H_4O_6$, and why?
3. Why cannot K^+ be detected by the action of $Na_3[Co(NO_2)_6]$ in alkaline solution? Describe the procedure for this reaction if the solution contains an excess of a strong acid.
4. State the conditions for detection of Na^+ by the action of KH_2SbO_4. What is the action of acids and of ammonium salts on this reagent?
5. What are the tests for the ammonium ion? How is it removed from solution, and why?
6. What reactions distinguish Mg^{++} from the other Group I cations? Why is it included in Group I and not II?
7. Write down the equation for the reaction of Mg^{++} with disodium hydrogen phosphate in the presence of NH_4OH. Why is NH_4Cl added in this test?
8. Can alkalies be used for detection of the Mg^{++} ion? Which Group I cations may interfere with this reaction?
9. How is Mg^{++} separated from the other Group I cations? What is the purpose of the separation? Can it be performed before the removal of ammonium salts?
10. Which Group I cations interfere with detection of K^+? Which Group I cations interfere with detection of Na^+ by the reaction with KH_2SbO_4?
11. Devise a procedure for systematic analysis of a mixture of all Group I cations if the only reagent available for Na^+ is KH_2SbO_4.
12. What should be added to neutralize acid solutions before detection of (a) K^+; (b) Na^+?
13. An analyst did not check whether ammonium salts had been completely removed in the course of analysis. To what errors in the analytical results may this lead?
14. State the wet-way reactions for Group I cations which could be used for analysis of mixtures by the fractional method.

CHAPTER III

CATIONS OF GROUP II

THEORETICAL ASPECTS

In our study of cation Group II (as well as Groups III to V) we will meet numerous instances where insoluble compounds of individual ions and of whole groups of ions are precipitated. In order to be able to control this most important operation of qualitative analysis, we must understand the theory of precipitation and of the opposite process—the dissolution of precipitates. Accordingly, these theoretical aspects of qualitative analysis are discussed in the present chapter together with the reactions and analytical procedure for the cations of Group II.

24. Solubility Product

In Sections 11 and 12 we examined some examples of ionic equilibria in electrolyte solutions. These solutions are *homogeneous* systems. In analytical practice we also deal with the more complex *heterogeneous* systems, such as systems consisting of saturated solutions in contact with their precipitates.

The distinct parts of a heterogeneous system, with definite bounding surfaces or interfaces between them, are known as its *phases*. For example, the precipitate and the saturated solution are different phases of a heterogeneous system of the kind described above.

It is evident that in analytical precipitation reactions we are concerned with just this type of heterogeneous systems; therefore study of such systems is of great importance for analytical chemistry, and we must examine them in detail.

Suppose that a sparingly soluble salt, such as AgCl, is brought into contact with water. The Ag^+ and Cl^- ions forming its crystals are attracted by the nearest water dipoles, are gradually detached from the crystal surfaces, and pass into solution in the form of hydrated ions. This dissolution process is accompanied by the opposite process of AgCl precipitation. Here the hydrated Ag^+ and Cl^- ions, moving in the solution, collide with the surfaces of the AgCl crystals and are attracted by the oppositely charged ions in the crystal lattice. In some instances they become dehydrated and redeposited on the crystal surfaces. This is represented schematically in Fig. 15.

As always, the occurrence of these two opposing processes leads to a state of dynamic equilibrium, when the number of Ag^+ and Cl^- ions leaving unit area of the solid phase in unit time is exactly

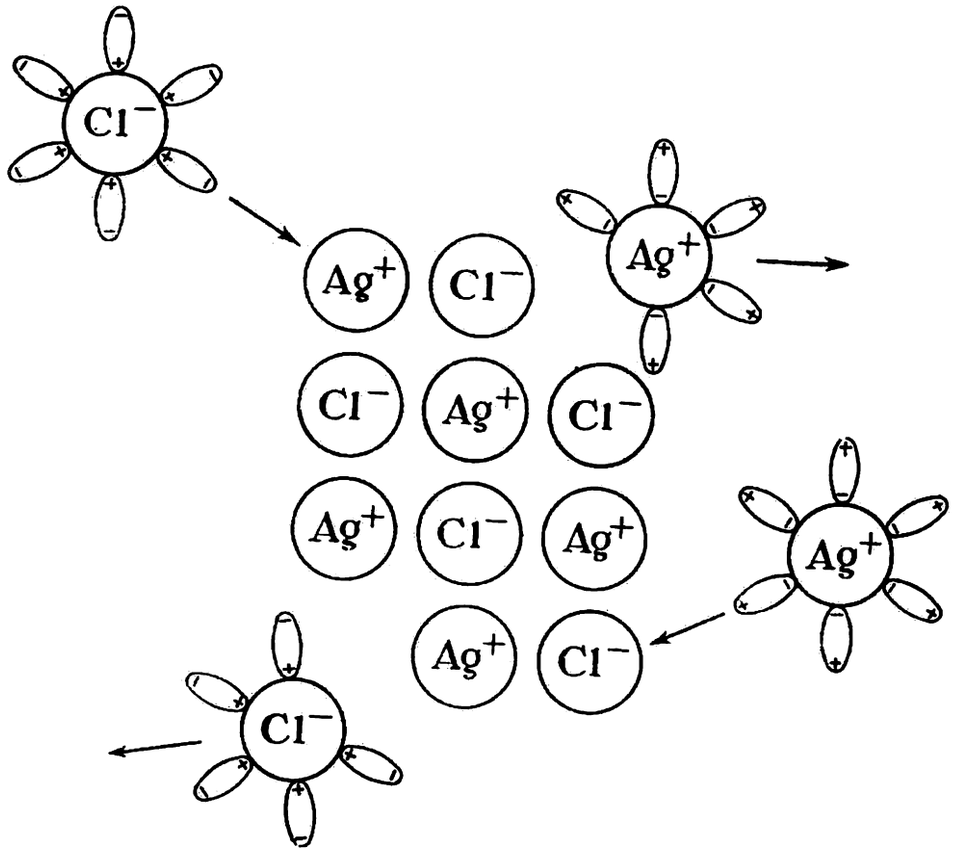


Fig. 15. Dissolution of AgCl (schematic)

equal to the number deposited from solution. When this equilibrium state is reached, the amounts of Ag^+ and Cl^- ions in solution cease to increase and the amount of solid phases ceases to diminish, and a saturated solution is obtained. Therefore a *saturated solution is one in dynamic equilibrium with its solid phase.*

To derive the general law governing this equilibrium, we write the expressions for the rates of transfer of Ag^+ and Cl^- ions into solution (v_1) and the rate of their deposition on the AgCl crystal surfaces (v_2).

The rate v_1 (i.e., the amount of Ag^+ and Cl^- ions passing into solution from unit area of the solid phase per unit time) is proportional to the number of ions per unit area of the solid surfaces. It may be assumed that this number of ions does not alter with time. Therefore the rate of dissolution may be regarded as constant at a given temperature:

$$v_1 = k_1$$

The rate v_2 of the deposition of Ag^+ and Cl^- ions on the AgCl crystals depends on the number of collisions of Ag^+ and Cl^- ions with unit area of the solid surface per unit time. In the absence of interionic forces in solution, decreasing the speeds of the ions (and consequently the number of collisions), the number of collisions would be proportional to the Ag^+ and Cl^- ion concentrations in solution. To take these forces into account we must evidently use ion activities rather than their concentrations. Therefore

$$v_2 = k_2 \cdot a_{Ag^+} \cdot a_{Cl^-}$$

where k_2 is a proportionality factor, constant at constant temperature.

At equilibrium $v_2 = v_1$, i.e.,

$$k_2 \cdot a_{Ag^+} \cdot a_{Cl^-} = k_1$$

$$a_{Ag^+} \cdot a_{Cl^-} = \frac{k_1}{k_2} = SP_{AgCl} \qquad (1)$$

Thus, *the product of the ion activities of a given sparingly soluble electrolyte in saturated solution is constant at constant temperature.* As this constant is a measure of the ability of a substance to dissolve, it is known as the *solubility product*, denoted in this book by *SP**.

Strictly speaking the assumption that the number of Ag^+ and Cl^- ions per unit area of the solid phase surface is constant is not quite true.

The reason is that in the course of precipitation the crystals always adsorb (i.e., retain on their surfaces) the common ion (Ag^+ and Cl^-) present in solution in excess. Since the amount of ions adsorbed depends on their concentration in solution, the amounts of Ag^+ and Cl^- ions per unit area of the solid phase vary somewhat with these concentrations. However, it is easy to show that these variations do not affect the final result.

Consider the equilibrium conditions for each of the ions separately.

1. The rate of transfer of Ag^+ ions (v_1) into solution is proportional to the number of these ions per unit area of the solid phase (n_1), i.e.,

$$v_1 = k_1 \cdot n_1$$

The rate of deposition of the Ag^+ ions is proportional to:

(a) the number of collisions between the Ag^+ ions with unit area of the solid phase per unit time, and therefore to a_{Ag^+};

(b) the number of Cl^- ions (attracting Ag^+ ions) per unit area (n_2); hence

$$v_2 = k_2 \cdot n_2 \cdot a_{Ag^+}$$

At equilibrium $v_1 = v_2$, i.e.,

$$k_1 \cdot n_1 = k_2 \cdot n_2 \cdot a_{Ag^+} \qquad (2)$$

2. Similarly, the rate of transfer of Cl^- ions into solution (v_3) is

$$v_3 = k_3 \cdot n_2$$

* The symbols *Lp*, *L* or *Sp* are also sometimes used.

The rate (v_4) at which these ions are deposited on the surface of the solid phase is

$$v_4 = k_4 \cdot n_1 \cdot a_{Cl^-}$$

At equilibrium $v_3 = v_4$ or

$$k_3 \cdot n_2 = k_4 \cdot n_1 \cdot a_{Cl^-} \quad (3)$$

Multiplying together the two partial expressions (2) and (3) for the individual ions we derive the general equilibrium equation for the system as a whole:

$$k_1 \cdot n_1 \cdot k_3 \cdot n_2 = k_2 \cdot n_2 \cdot a_{Ag^+} \cdot k_4 \cdot n_1 \cdot a_{Cl^-}$$

The quantities n_1 and n_2, present in both sides of the equation, cancel out. Therefore, whatever the amounts of Ag^+ and Cl^- ions per unit area of the AgCl crystal, and whatever their variations during precipitation, the final result is not affected.

If we move the constants k_2 and k_4 to the left-hand side of the equation, we have

$$\frac{k_1 \cdot k_3}{k_2 \cdot k_4} = a_{Ag^+} \cdot a_{Cl^-}$$

If we now put SP_{AgCl} for the ratio $\frac{k_1 \cdot k_3}{k_2 \cdot k_4}$, we obtain Equation (1) as given above.

If the coefficients relating to the different ions in the dissociation equation of an electrolyte are not unity, their activities are raised to the corresponding powers in the expression for the solubility product; for example:

$$SP_{Ca_3(PO_4)_2} = a^3_{Ca^{++}} \cdot a^2_{PO_4^{---}}$$

Since the activity of an ion is its concentration multiplied by the activity coefficient (see p. 63), the expression for SP_{AgCl} may be written as follows:

$$SP_{AgCl} = [Ag^+] \cdot [Cl^-] \cdot f_{Ag^+} \cdot f_{Cl^-}$$

Since the solubility of AgCl is very slight, the ion concentration in a saturated solution is very low and the effect of interionic forces is negligible. Therefore we may assume, without appreciable error, that f_{Ag^+} and f_{Cl^-} are equal to unity. This gives the approximate equation

$$SP_{AgCl} \approx [Ag^+] \cdot [Cl^-]$$

and this is generally used in practice.

In the case of a readily soluble electrolyte the activity coefficients of the ions are not unity and therefore we cannot use ion concentrations in place of activities. Neither is this permissible for sparingly soluble electrolytes such as AgCl if other strong electrolytes are also present in solution. However, calculations based on the solubility product rule do not usually require a high degree of accuracy and it is inconvenient to use activities. Therefore in most cases concentra-

tions are used instead of activities even in the presence of strong electrolytes, and the consequent error is neglected.

Despite this simplification, the solubility product rule is of very great importance in analytical chemistry. This rule enables us to interpret many quite complex problems arising in analytical practice, and the conclusions are nearly always in *qualitative* agreement with experiment. We shall therefore use the solubility product rule in its simplified form, without activity coefficients, using the latter only when absolutely necessary.

To find the solubility product of a sparingly soluble electrolyte we must determine its solubility experimentally at the given temperature by a suitable method. It is then easy to calculate SP*. This is illustrated by the following examples.

Example 1. Calculate SP_{AgCl}, given that a saturated solution of AgCl at 25° contains 0.0018 (i.e., 1.8×10^{-3}) g of the salt per litre.

Solution. First find the molar concentration of the saturated AgCl solution. As the molecular weight of AgCl is 143.3, we have

$$c_{AgCl} = \frac{1.8 \times 10^{-3}}{143.3} = 1.25 \cdot 10^{-5} \text{ mole/litre}$$

As each gram-molecule of AgCl gives rise to a gram-ion each of Ag^+ and Cl^-, this value also gives their concentrations in saturated AgCl solutions. Therefore

$$SP_{AgCl} = [Ag^+] \cdot [Cl^-] = 1.25 \times 10^{-5} \times 1.25 \times 10^{-5} = 1.56 \times 10^{-10}$$

Example 2. Calculate the solubility product of silver chromate ($SP_{Ag_2CrO_4}$), given that 1 litre of a saturated solution at 25° contains about 4.3×10^{-2} g of the salt.

Solution.

$$c_{Ag_2CrO_4} = \frac{4.3 \times 10^{-2}}{331.8} \approx 1.3 \times 10^{-4} \text{ mole/litre}$$

Since each gram-molecule of Ag_2CrO_4 dissolves to give 1 g-ion of CrO_4^{--} and 2 g-ions of Ag^+, we have

$$[CrO_4^{--}] = 1.3 \times 10^{-4} \text{ g-ion/litre}$$

$$[Ag^+] = 2.6 \times 10^{-4} \text{ g-ion/litre}$$

and hence

$$SP_{Ag_2CrO_4} = [Ag^+]^2 \cdot [CrO_4^{--}] = (2.6 \times 10^{-4})^2 \times 1.3 \times 10^{-4} = 9 \times 10^{-12}$$

Note that although the solubility of AgCl (1.25×10^{-5}) is lower than that of Ag_2CrO_4 (1.3×10^{-4}), the solubility product of AgCl (1.56×10^{-10}) is higher than that of Ag_2CrO_4 (9×10^{-12}). This is because in calculating $SP_{Ag_2CrO_4}$ we have to square a small quantity,

---

* If the solubility of the electrolyte is not low enough for the interionic forces to be disregarded, for calculation of SP it is necessary to calculate the ionic strength μ of the solution and then to find the activity coefficients of the ions from it. The calculation is shown in Example 1 (b), on pp. 120-121.

the Ag^+ concentration (2.6×10^{-4}). Therefore the solubility products of electrolytes can be used for comparing their solubilities only if their formulas are of the same type; for example, AgCl, $BaSO_4$ and $CaCO_3$, or Ag_2CrO_4, Ag_2CO_3, PbI_2, etc.

Example 3. The solubility of $CaSO_4$ at room temperature is 2 g/litre. Calculate SP_{CaSO_4}.

Solution. The difference between this and the preceding examples is that the solubility of $CaSO_4$ is so high that the activity coefficients of the ions cannot be taken as unity. To find them, we first calculate the ionic strength of the solution. The molar concentration of the saturated solution is

$$c_{CaSO_4} = \frac{2}{136} = 0.015 = 1.5 \times 10^{-2}\, M$$

Therefore

$$[Ca^{++}] = [SO_4^{--}] = 1.5 \times 10^{-2} \text{ g-ion/litre}$$

and

$$\mu = \frac{1}{2}\,([Ca^{++}] \times 2^2 + [SO_4^{--}] \times 2^2) = \frac{1}{2}\,(1.5 \times 10^{-2} \times 4 + 1.5 \times 10^{-2} \times 4) = 0.06$$

From Table 6 (p. 65) we have

$$f_{Ca^{++}} = f_{SO_4^{--}} = 0.44$$

Consequently*

$$SP_{CaSO_4} = [Ca^{++}] \cdot [SO_4^{--}] \cdot f_{Ca^{++}} \cdot f_{SO_4^{--}} = (1.5 \times 10^{-2} \times 0.44)^2 = 4 \times 10^{-5}$$

It is quite obvious that it is easy to solve the converse problem—to calculate the solubility of an electrolyte in moles or grams per litre if the solubility product is known.

Example 4. Find the solubility of $Mg(OH)_2$ at 25°, given that its solubility product is 5×10^{-12}.

Solution. Let the required solubility in moles per litre be x. A solution of x moles of $Mg(OH)_2$ contains the following ion concentrations:

$$[Mg^{++}] = x; \quad [OH^-] = 2x$$

hence

$$SP_{Mg(OH)_2} = [Mg^{++}] \cdot [OH^-]^2 = x \cdot (2x)^2 = 5 \times 10^{-12}$$

or

$$4x^3 = 5 \times 10^{-12} \text{ and } x = \sqrt[3]{1.25 \times 10^{-12}} \approx 1.1 \times 10^{-4} \text{ mole/litre}$$

To express the solubility in grams per litre, we multiply the result by 58.3, the molecular weight of $Mg(OH)_2$. This gives

$$y = 1.1 \times 10^{-4} \times 58.3 \approx 6.4 \times 10^{-3} \text{ g/litre}$$

---

* This result differs from 6.1×10^{-5}, the experimental value for SP_{CaSO_4}, because Table 6 gives average values of the activity coefficients, which in reality are different for different ions. Without the activity coefficients being taken into account the calculated value for SP_{CaSO_4} is 2.25×10^{-4}, which differs greatly from the experimental value.

Example 5. Given that the solubility product of $AgBrO_3$ at 25° is 5.77×10^{-5}, calculate its solubility.

Solution. This differs from the previous example because here the solubility product is relatively large, so that activity coefficients cannot be disregarded. To calculate the ionic strength of the solution, we first find the approximate ion concentrations from the simplified formula

$$SP_{AgBrO_3} \approx [Ag^+]\cdot[BrO_3^-]$$

Since $[Ag^+] = [BrO_3^-]$, we have

$$[Ag^+]=[BrO_3^-]=\sqrt{5.77\times10^{-5}}=7.59\times10^{-3}\approx0.008 \text{ g-ion/litre}$$

Therefore

$$\mu=\frac{1}{2}(0.008\times1^2+0.008\times1^2)=0.008$$

From Table 6 (Sec. 14) we have

$$f_{Ag^+}=f_{BrO_3^-}=0.90$$

From this we can find the solubility of $AgBrO_3$ more accurately. Denoting it by x, and remembering that $[Ag^+] = [BrO_3^-] = x$, we have

$$[Ag^+]\cdot[BrO_3^-]\cdot f_{Ag^+}\cdot f_{BrO_3^-}=x^2\cdot0.90^2=5.77\times10^{-5}$$

and hence

$$x=\frac{\sqrt{5.77\times10^{-5}}}{0.90}=\frac{7.59\times10^{-3}}{0.90}=8.4\times10^{-3} \text{ mole/litre}$$

From this we find the solubility in grams per litre:

$$y=8.4\times10^{-3}\times235.8=1.98 \text{ g/litre}$$

If we had not taken the activity coefficients into account in calculating the solubility, we would have found

$$y=7.59\times10^{-3}\times235.8=1.79 \text{ g/litre}$$

The solubility products of the most important sparingly soluble electrolytes are given in Table IV (see Appendix).

25. Influence of Common Ions on Solubility. The Salt Effect

According to the solubility product rule, *at the point when the product of the concentrations (or, more accurately, the activities) of the ions (the "ionic product") of a sparingly soluble electrolyte reaches the value of its solubility product at the given temperature, the solution becomes saturated with respect to that electrolyte.*

Conversely, if the ionic product is less than the solubility product the concentration of the solution is lower than at saturation, and the solution is unsaturated.

It is also easy to see that if the ionic product exceeds the solubility product the solution becomes supersaturated and must sooner or later deposit a part of the solute as a solid phase (precipitate).

By increasing the electrolyte ion concentration we raise the rate at which the ions are deposited on the solid phase surface. When the ionic product reaches the SP value, the rates of dissolution and precipitation become equal. If the ionic product increases further, above the solubility product, precipitation prevails over dissolution and a precipitate must be deposited from the solution. For example, for AgCl we have:

in unsaturated solution

$$[Ag^+]\cdot[Cl^-] < SP_{AgCl}$$

in saturated solution

$$[Ag^+]\cdot[Cl^-] = SP_{AgCl}$$

in supersaturated solution

$$[Ag^+]\cdot[Cl^-] > SP_{AgCl}$$

From this it is clear that by adding an electrolyte with a common ion to an unsaturated solution of any electrolyte we can make the solution saturated and even supersaturated.

For example, if we slowly add HCl or KCl to an unsaturated AgCl solution, the ionic product, initially less than SP_{AgCl} (i.e., $< 1.56 \times 10^{-10}$ at 25°) gradually reaches and then exceeds this value. Correspondingly, the unsaturated solution becomes saturated and then supersaturated.

It follows from the foregoing that *the solubility of a sparingly soluble electrolyte is lowered by addition of an electrolyte with a common ion to its solution.*

To confirm this experimentally, let us take a more soluble salt, such as $KClO_3$, instead of AgCl; the effect of the common ion is then more pronounced.

Add concentrated KCl or $NaClO_3$ solution slowly to a saturated $KClO_3$ solution, stirring continuously. After some time a white crystalline precipitate forms; this is found to be $KClO_3$.

Thus, in agreement with the solubility product rule, the solubility of $KClO_3$ in the presence of KCl or $NaClO_3$ is lower than in pure water. The same is found in analogous cases.

Experiment shows that the solubility of electrolytes is influenced not only by salts with a common ion but also by salts without such ions; in the latter case the solubility is usually increased. For example, I. V. Tananaev and I. B. Mizetskaya found that the solubility of $PbSO_4$ is raised in the presence of salts such as KNO_3, $NaNO_3$, etc., and this effect, known as the *salt effect*, increases with the concentration of the added salt.

When we add KNO_3 or $NaNO_3$ we are not introducing ions which might combine with Pb^{++} or SO_4^{--} ions [since $Pb(NO_3)_2$, K_2SO_4

and Na_2SO_4 are all strong electrolytes], the increased solubility of $PbSO_4$ cannot be explained by the solubility product rule in its simplified form:

$$[Pb^{++}]\cdot[SO_4^{--}] = SP_{PbSO_4}$$

However, it is easily explained if we use the exact equation

$$[Pb^{++}]\cdot[SO_4^{--}]\cdot f_{Pb^{++}}\cdot f_{SO_4^{--}} = SP_{PbSO_4}$$

more conveniently written in the form

$$[Pb^{++}]\cdot[SO_4^{--}] = \frac{SP_{PbSO_4}}{f_{Pb^{++}}\cdot f_{SO_4^{--}}}$$

In this equation SP_{PbSO_4} is strictly constant. The activity coefficients $f_{Pb^{++}}$ and $f_{SO_4^{--}}$ are usually decreased by the introduction of any ions whatever, because of the increased interionic forces (the "ionic strength" of the solution). Therefore, in agreement with experiment, the product $[Pb^{++}]\cdot[SO_4^{--}]$, and therefore the solubility of lead sulphate increases.

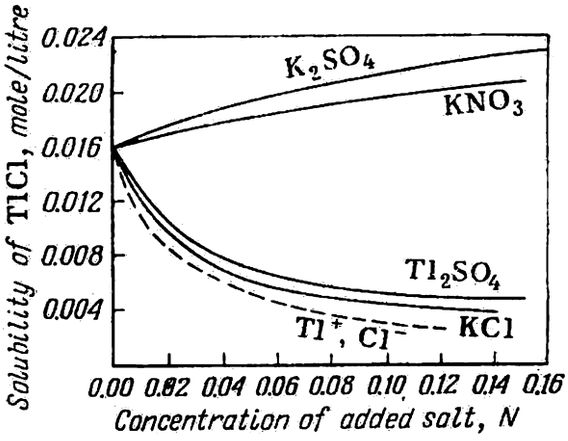


Fig. 16. Solubility of TlCl in the presence of extraneous and common ions

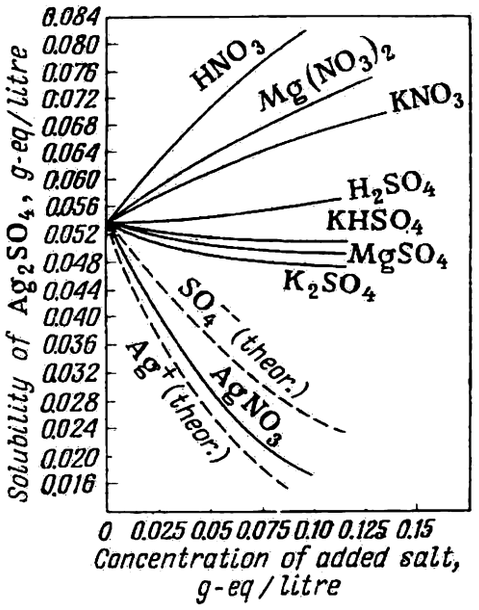


Fig. 17. Solubility of Ag_2SO_4 in the presence of extraneous and common ions

The physical reason for this is easily understood; the Pb^{++} and SO_4^{--} ions, restricted in their movement by interionic forces, collide less frequently with the surfaces of the $PbSO_4$ crystals. In consequence dissolution of these crystals prevails over the deposition of ions from solution.

It is obvious that the activity coefficients of the ions should also decrease when an electrolyte with a common ion is added to the solution, i. e., the salt effect should also occur in such a case. However, it is usually masked by the opposing influence of the common ion on the solubility, and may be disregarded when we consider the effect *qualitatively*. Quantitative investigations show that in such cases the observed lowering of the solubility is less than calculated from the solubility product rule in its simplified form.

This is illustrated by the graph (Fig. 16) showing the influence of various electrolytes on the solubility of TlCl. In the presence of Tl_2SO_4 and KCl the solubility of TlCl decreases, but the decrease is somewhat less than is given by calculation from the simplified equation for SP_{TlCl}, i. e., without account being taken of the activity coefficient (broken curve). On the other hand, in the presence of salts without a common ion the solubility is raised (the salt effect). The effect is greater with K_2SO_4, yielding the bivalent ion SO_4^{--}, than with KNO_3 which gives only univalent ions. Similar relationships are illustrated in Fig. 17 for Ag_2SO_4 solutions.

The following numerical examples illustrate the above discussion.

Example 1. Calculate the solubility of barium iodate, $Ba(IO_3)_2$, in 0.03 *M* $Ba(NO_3)_2$ solution (a) approximately, and (b) with activity coefficients taken into account.

Solution. (a) First use the simplified formula for the solubility product for the approximate calculation. Start by calculating $SP_{Ba(IO_3)_2}$, given that the concentration of a saturated solution (at 25°) is 0.0008 *M*. Assuming that the salt is completely dissociated to give two IO_3^- ions for every Ba^{++} ion, we have

$$SP_{Ba(IO_3)_2} = [Ba^{++}] \cdot [IO_3^-]^2 = 0.0008 \times (0.0016)^2 = 2.05 \times 10^{-9}$$

Denote the required solubility of $Ba(IO_3)_2$ in the presence of barium nitrate by x (in moles per litre). Then the concentration of IO_3^- ions in the solution is $2x$. The concentration of the Ba^{++} ions is given by the sum of the ion concentrations resulting from dissociation of $Ba(NO_3)_2$ (0.03 *M*) and from dissolution of the precipitate (x).

Therefore we can write

$$[Ba^{++}] \cdot [IO_3^-]^2 = (0.03 + x) \times (2x)^2 = 2.05 \times 10^{-9}$$

Since x is very small, it may be neglected by comparison with 0.03. We then have:

$$0.12x^2 = 2.05 \times 10^{-9} \text{ or } x = \sqrt{1.708 \times 10^{-8}} = 1.31 \times 10^{-4} = 0.000131 \ M$$

Thus, according to the simplified form of the solubility product rule, the solubility of $Ba(IO_3)_2$ in 0.03 *M* barium nitrate solution should be 0.000131 *M*, as compared with 0.0008 *M* in water; this is approximately a sixfold decrease.

(b) Now use the exact formula

$$a_{Ba^{++}} \cdot a^2_{IO_3^-} = SP_{Ba(IO_3)_2}$$

First find the more precise value of $SP_{Ba(IO_3)_2}$, replacing Ba^{++} and IO_3^- ion concentrations by their activities in solution. To do this, multiply the ion con-

centrations by their activity coefficients. The latter depend on the ionic strength of the solution. The ionic strength of a saturated aqueous solution of barium iodate is

$$\mu=\frac{1}{2}\times(0.0008\times 2^2+0.0016\times 1^2)=0.0024$$

From the activity coefficients given on p. 65 we find by interpolation* that this ionic strength corresponds to the following activity coefficients:

$$f_{Ba^{++}}=0.81 \text{ and } f_{IO_3^-}=0.95$$

And so we have

$$a_{Ba^{++}}=0.0008\times 0.81 \text{ and } a_{IO_3^-}=0.0016\times 0.95$$

The accurate value of $SP_{Ba(IO_3)_2}$ is

$$SP_{Ba(IO_3)_2}=(0.0008\times 0.81)\times(0.0016\times 0.95)^2=1.49\times 10^{-9}$$

Use this value to calculate the solubility of $Ba(IO_3)_2$ in 0.03 *M* $Ba(NO_3)_2$ solution. To do this, re-calculate the ionic strength of the solution. Since $Ba(IO_3)_2$ yields very few ions in solution by comparison with $Ba(NO_3)_2$, only the latter need be taken into account in calculating the ionic strength. Therefore

$$\mu=\frac{1}{2}(0.03\times 2^2+0.06\times 1^2)=0.09$$

This corresponds to the following activity coefficients:

$$f_{Ba^{++}}=0.35 \quad \text{and} \quad f_{IO_3^-}=0.79$$

Denoting the required molar concentration of the saturated $Ba(IO_3)_2$ solution by x and remembering that $[IO_3^-] = 2x$, we have

$$SP_{Ba(IO_3)_2}=a_{Ba^{++}}\cdot a^2_{IO_3^-}=(0.03\times 0.35)\times(2x\times 0.79)^2=1.49\times 10^{-9}$$

and

$$x=0.00024\ M$$

Thus, in the presence of 0.03 mole $Ba(NO_3)_2$ per litre the solubility of barium iodate falls from 0.0008 *M* to 0.00024 *M*, which is a factor of approximately 3 (as compared with the factor of 6 given by the approximate calculation).

Example 2. Calculate the solubility of barium iodate in 0.1 *M* KNO_3 solution.

---

* This is done as follows. The value $\mu = 0.0024$ is between 0.001 and 0.005. The difference between these two is 0.004. Table 6 shows that this difference of μ corresponds to a decrease of f from 0.86 to 0.72, or 0.14, for bivalent ions.

By proportion

0.004 is to 0.14

as 0.0014 is to x

hence

$$x=\frac{0.0014\times 0.14}{0.004}=0.05$$

which gives

$$f_{Ba^{++}}=0.86-0.05=0.81$$

Solution. As before, the ionic strength of the solution is determined only by the presence of potassium nitrate, and has the value

$$\mu = \frac{1}{2}(0.1 \times 1^2 + 0.1 \times 1^2) = 0.1$$

This corresponds to

$$f_{Ba^{++}} = 0.33 \text{ and } f_{IO_3^-} = 0.78$$

Hence we have

$$(0.33 \cdot x) \cdot (0.78 \cdot 2x)^2 = 1.50 \times 10^{-9} \text{ and } x = 0.00123 \ M$$

Therefore the presence of 0.1 mole of a salt (KNO_3) which does not have a common ion with $Ba(IO_3)_2$ raises the solubility of barium iodate from 0.0008 *M* to 0.00123 *M*, which is a factor of about 1.5 (the salt effect).

26. Formation of Precipitates

We showed above that the effects of common ions on the solubility of precipitates can be predicted with the aid of the solubility product rule.

The rule is especially useful when applied to cases where a precipitate forms or dissolves as the result of a chemical reaction.

Suppose, for example, that a solution of a lead salt is mixed with a soluble chloride. As a result, Pb^{++} ions meet Cl^- ions and the formation of a $PbCl_2$ precipitate is possible. However, precipitation will actually occur only if the solution becomes supersaturated with the salt. We know that it will become supersaturated only if the ionic product $[Pb^{++}] \cdot [Cl^-]^2$ exceeds 2.4×10^{-4}, which is the solubility product of $PbCl_2$ (at 25°). From this we can predict theoretically whether lead chloride will be precipitated under given conditions. The following examples illustrate the foregoing.

Example 1. Does a precipitate form when equal volumes of 0.1 *M* $Pb(NO_3)_2$ and NaCl solutions are mixed?

Solution. When the solutions are mixed the total volume is doubled and the concentration of each component falls to 0.05 or 5×10^{-2} *M*. These must also be the concentration of Pb^{++} and Cl^- ions at the instant when the solutions are mixed. Therefore the ionic product must be

$$[Pb^{++}] \cdot [Cl^-]^2 = 5 \times 10^{-2} \times (5 \times 10^{-2})^2 = 125 \times 10^{-6} = 1.25 \times 10^{-4}$$

As this is less than the solubility product of $PbCl_2$ (2.4×10^{-4}) at the given temperature (25°), the solution is unsaturated and $PbCl_2$ cannot be precipitated.

Example 2. Suppose that 0.1 *M* $Pb(NO_3)_2$ solution is mixed with an equal volume of 1 *M* NaCl. Does a precipitate form?

Solution. The ion concentrations at the instant of mixing are

$$[Pb^{++}] = 5 \times 10^{-2} \text{ g-ion/litre; } [Cl^-] = 0.5 = 5 \times 10^{-1} \text{ g-ion/litre}$$

And in this case the ionic product is

$$[Pb^{++}] \cdot [Cl^-]^2 = 5 \times 10^{-2} (5 \times 10^{-1})^2 = 125 \times 10^{-4} = 1.25 \times 10^{-2}$$

This is much greater than the solubility product of $PbCl_2$ (2.4×10^{-4}). The solution therefore becomes supersaturated with this salt and a part of it is precipitated.

These results are fully substantiated by experiment. If we mix equal volumes of 0.1 *M* lead nitrate and sodium chloride solutions, no precipitate forms. If we repeat the experiment using 1 *M* NaCl instead of 0.1 *M*, an abundant white precipitate of $PbCl_2$ is formed on shaking. These experiments clearly demonstrate the great importance of the concentration of the precipitant (in this case NaCl) in precipitation reactions. The higher the concentration, the greater is the sensitivity of the reaction in most cases (some limitations of this rule are discussed below).

The following general conclusion may be drawn from all the foregoing: *any sparingly soluble electrolyte is precipitated only if the product of the concentrations of its ions (the "ionic product") in solution exceeds its solubility product at the given temperature.*

We now consider the completeness of precipitation and the factors which influence it.

It is evident that when the precipitation of an ion has started it continues until the ionic product, which gradually decreases, becomes equal to the solubility product of the precipitate. At this instant equilibrium is established between the precipitate and the solution and the amount of precipitate ceases to increase.

Since no substances are completely insoluble in water, the solubility product is never zero. For example, Table IV (Appendix) shows that even one of the most insoluble substances, mercuric sulphide (HgS), has a measurable although extremely small solubility product; its value is 4.0×10^{-53}. It follows that, strictly speaking, *no precipitation can ever be quite complete.* Some of the ions, corresponding to the solubility product of the precipitated compound, always remain in solution. Sometimes this residual part is so small that it does not interfere with the subsequent analysis. In such cases the precipitation may be termed *practically complete.* However, cases when the precipitation is not complete even practically are quite common. In such cases the analyst must take steps to achieve practically complete precipitation.

Completeness of precipitation is an exceptionally important matter in analytical chemistry, as the aim of every ion separation in qualitative analysis—the elimination of the interfering effects of the separated ions in subsequent analysis—is achieved only if the precipitation is practically complete. We shall therefore consider more fully the factors on which the completeness of precipitation depends.

1. Solubility of the compound precipitated. It is obvious that the lower the solubility of the precipitated compound containing the

given ion, the more complete is the separation under given conditions. For example, Pb^{++} may be precipitated as the chloride, sulphate, or sulphide.

The solubilities and solubility products of these salts are:

	$PbCl_2$	$PbSO_4$	PbS
Solubility, moles/litre	3.9×10^{-2}	1.5×10^{-4}	3.3×10^{-15}
Solubility product	2.4×10^{-4}	2.2×10^{-8}	1.1×10^{-29}

These figures show that the chloride is the most soluble and the sulphide is the least soluble of these lead compounds. Therefore lead can be precipitated most completely as PbS and least so as $PbCl_2$.

This can be easily confirmed by experiment. Mix 10 ml of 1 *N* $Pb(NO_3)_2$ with about 11 ml of 1 *N* NaCl, shake vigorously, and filter off the $PbCl_2$ precipitate. Test the filtrate for completeness of precipitation (by adding one or two drops of NaCl) and divide it into two parts. Add a little $(NH_4)_2S$ solution to one and Na_2SO_4 solution to the other. A black PbS precipitate is formed in the first case, and a white $PbSO_4$ precipitate in the second. The latter usually appears only after vigorous shaking (precipitation from supersaturated solution).

In the same way it is easy to show that the precipitation of Pb^{++} is more complete as PbS than as $PbSO_4$. To 10 ml of 1 *N* $Pb(NO_3)_2$ add about 11 ml of 1 *N* Na_2SO_4, filter off the precipitated $PbSO_4$, check for completeness of precipitation, and add $(NH_4)_2S$ solution to the filtrate. The liquid turns dark brown* owing to the formation of a small amount of PbS.

These experiments clearly illustrate the different degrees of precipitations attained when a given ion is converted into sparingly soluble compounds having different solubility products. It should be remembered, however, that in this case the solubility of the precipitate in moles per litre gives a better indication than the solubility product. For example, it was pointed out on p. 115 that the solubility of AgCl (1.25×10^{-5} *M*) is less than that of Ag_2CrO_4 (1.3×10^{-4} *M*), although the solubility product of silver chloride (1.56×10^{-10}) is greater than that of silver chromate (9×10^{-12}). In accordance with the lower solubility of silver chloride the precipitation of Ag^+ under given conditions is more complete in the form of AgCl than as Ag_2CrO_4.

2. Amount of precipitating reagent added. For practically complete precipitation of any ion the amount of precipitant added must evi-

---

* Lead sulphide is sometimes formed in the form of a sol. If a little NH_4Cl solution (coagulant electrolyte) is added to the sol and the liquid is heated to boiling, PbS is coagulated and precipitated in the form of black flakes.

dently be not less than required in accordance with the reaction equation, i. e., not less than the amount equivalent to the amount of the ion to be precipitated. However, if the solubility product is not too small, the addition of equivalent amount of precipitant does not usually result in practically complete precipitation. Nevertheless, the solubility product rule shows that the precipitation becomes more complete if we introduce the precipitant in some excess. Since the ionic product $[Pb^{++}] \cdot [SO_4^{--}]$ remains (approximately) constant during precipitation of $PbSO_4$ at a value equal to SP_{PbSO_4}, it follows that an increase of the SO_4^{--} ion concentration due to addition of excess precipitant (Na_2SO_4 or H_2SO_4) leads to a corresponding decrease of the Pb^{++} ion concentration in solution, i. e., it makes the precipitation of the lead ion more complete. Therefore *if the reaction used for separating a particular ion involves the formation of a compound which is appreciably soluble in water, the precipitant is taken in some excess, i. e., more is taken than the reaction equation requires.*

Since $[Pb^{++}] \cdot [SO_4^{--}] = SP_{PbSO_4}$, it might be thought that the more H_2SO_4 we add the more complete the precipitation of Pb^{++} must be. However, this is not the case in fact. A very large excess of sulphuric acid even raises the solubility of the precipitate owing to the formation of acid lead sulphate:

$$PbSO_4 + H_2SO_4 = Pb(HSO_4)_2$$

Similarly, in the reaction

$$Hg(NO_3)_2 + 2KI = \downarrow HgI_2 + 2KNO_3$$

if too large an excess of KI is added the precipitate dissolves completely owing to the formation of the complex compound $K_2[HgI_4]$:

$$HgI_2 + 2KI = K_2[HgI_4]$$

Even if there are no grounds for expecting the formation of complex or acid salts, or of amphoteric compounds (in the precipitation of hydroxides), too large an excess of precipitant is undesirable for another reason. While an excess of precipitant lowers the solubility of the precipitate by raising the concentration of the precipitant ion, it tends to raise the solubility by intensifying the salt effect. When the excess of precipitant is not large, the increase of concentration prevails over the salt effect and the solubility of the precipitate falls. However, with too large an excess the reverse may be true, and the solubility may increase instead of decreasing.

For these reasons *the precipitant is never used in more than 50% excess in practice*; often even less is used.

3. The pH of the solution. The pH of the solution is usually of enormous importance in precipitation (Sec. 5). Let us consider more fully the influence of this factor in the precipitation of sparingly soluble hydroxides and salts of weak and strong acids.

Precipitation of Sparingly Soluble Metal Hydroxides. In this case OH^- is the precipitant ion, and its concentration increases with rise of the solution pH. It depends on the OH^- ion concentration whether the hydroxide is precipitated and whether the precipitation is practically complete. It is obvious that the greater the solubility of the hydroxide the higher is the OH^- ion concentration needed to exceed its solubility product, i. e., the higher the pH required for the start of precipitation.

The pH at which the precipitation of a particular hydroxide begins and ends can be approximately calculated from its solubility product. Let us do this calculation for magnesium hydroxide ($SP = 5 \times 10^{-12}$). If the Mg^{++} concentration in solution is 1×10^{-2} g-ion/litre, the equation

$$[Mg^{++}]\cdot[OH^-]^2 = SP_{Mg(OH)_2} = 5\times10^{-12}$$

gives the OH^- ion concentration at which the solubility product is reached and precipitation of $Mg(OH)_2$ begins. The required concentration is

$$[OH^-] = \sqrt{\frac{SP_{Mg(OH)_2}}{[Mg^{++}]}} = \sqrt{\frac{5\times10^{-12}}{1\times10^{-2}}} = 2.2\times10^{-5} \text{ g-ion/litre}$$

Consequently

$$pOH = -\log 2.2\times10^{-5} = -(0.3-5.0) = 4.7$$
$$pH = 14-pOH = 14-4.7 = 9.3$$

Therefore at pH = 9.3 the precipitation of $Mg(OH)_2$ begins in 0.01 *M* solution.

The precipitation of an ion may be regarded as complete when its concentration in solution has fallen to 10^{-5}-10^{-6} g-ion/litre. Taking the lower value (10^{-6}), we have for $[OH^-]$:

$$[OH^-] = \sqrt{\frac{5\times10^{-12}}{10^{-6}}} = 2.2\times10^{-3} \text{ g-ion/litre}$$

This corresponds to pOH = 2.7 and pH = 11.3.

If the pH is greater than 11.3, the precipitation of Mg^{++} is even more complete (i. e., the concentration of Mg^{++} ions remaining in solution falls to below 10^{-6} g-ion/litre). Conversely, at $pH < 11.3$ the precipitation of Mg^{++} is incomplete and at $pH \ll 9.3$ it does not occur at all. Thus, the precipitation of Mg^{++} as the hydroxide is complete if $pH \gg 11.3$.

A similar calculation for a much less soluble compound, ferric hydroxide, $Fe(OH)_3$ ($SP = 3.8 \times 10^{-38}$) shows that precipitation from a 0.01 *M* solution of a ferric salt begins at pH = 2.2 and is practically complete at pH $\geqslant$ 3.5.

The results of analogous calculations for a number of other sparingly soluble hydroxides usually met in analysis are given in Table 10. This table gives the pH values at which (a) hydroxide precipitation begins for metal cation concentrations of 1 and 1×10^{-2} g-ion per litre, and (b) at which precipitation is practically complete, corresponding to $c = 1 \times 10^{-6}$ g-ion/litre. The calculated values for the pH of the start of precipitation at $c = 1$ g-ion/litre are compared with the values found experimentally by Ya. A. Fialkov and N. V. Aksel'rud for $a = 1$ g-ion/litre. This comparison shows that in most cases the agreement between the theoretical calculations and the experimental values is fairly satisfactory, despite the fact that the activity coefficients of the ions were not taken into account in the calculations and that the solubility products of the hydroxides were not always determined with sufficient accuracy. This suggests that the pH values for practically complete precipitation of the hydroxides, not yet determined experimentally, should also be close to the calculated values given in Table 10.

Several important factors in analysis may be predicted from the data in Table 10. This may be illustrated by the following example. It was shown above that precipitation of $Mg(OH)_2$ from a 0.01 *M* solution of a magnesium salt begins at pH = 9.3. Since the pH of 0.1 *M* NH_4OH is 11.13 (see Example 7, Sec. 15), this solution should precipitate Mg^{++}; this is confirmed by experiment. However, if an equivalent amount of NH_4Cl is added to the NH_4OH solution an ammonium buffer mixture is formed. Its pH can be calculated from the equation (Sec. 16)

$$pH = 14 - pK_{base} + \log \frac{c_{base}}{c_{salt}}$$

For the present case this equation gives

$$pH = 14 - 4.75 + \log \frac{0.1}{0.1} = 9.25$$

Since the result (9.25) is less than the pH at which precipitation of $Mg(OH)_2$ begins (9.3), we must conclude that $Mg(OH)_2$ is not precipitated by this buffer mixture. This conclusion was confirmed in our study of the reactions of the Mg^{++} ion (Sec. 22-1). On the other hand, if we add the $NH_4OH + NH_4Cl$ mixture to a solution of $FeCl_3$, a precipitate of $Fe(OH)_3$ is formed, because the precipitation of this compound is complete at pH $\geqslant$ 3.5. This is also easily confirmed by experiment.

It is not difficult to understand why $Fe(OH)_3$ is precipitated while $Mg(OH)_2$ is not. The reason is evidently that the common NH_4^+ ions of NH_4Cl depress the degree of dissociation of NH_4OH

Table 10

Precipitation pH of Certain Hydroxides

Formula	Solubility product	Start of precipitation			Complete precipitation
		$c = 1$		$c=10^{-2}$	$c = 10^{-6}$
		exptl.*	calculated		
AgOH	2×10^{-8}	—	6.3	8.3	12.3
$Mg(OH)_2$	5×10^{-12}	—	8.3	9.3	11.3
$Mn(OH)_2$	4×10^{-14}	—	7.3	8.3	10.3
$Cd(OH)_2$**	1.2×10^{-14}	6.8	7.0	8.0	10.0
$Fe(OH)_2$	4.8×10^{-16}	6.6	6.3	7.3	9.3
$Co(OH)_2$**	2×10^{-16}	6.8	6.2	7.2	9.2
$Ni(OH)_2$**	6.3×10^{-16}	6.7	6.4	7.4	9.4
$Zn(OH)_2$	1×10^{-17}	5.8	5.5	6.5	8.5
$Cu(OH)_2$	5.6×10^{-20}	4.2	4.4	5.4	7.4
$Cr(OH)_3$	5.4×10^{-31}	—	3.9	4.6	5.9
$Bi(OH)_3$	4.3×10^{-31}	—	3.8	4.5	5.8
$Al(OH)_3$	1.9×10^{-33}	3.6	3.1	3.8	5.1
$Fe(OH)_3$	3.8×10^{-38}	1.6	1.5	2.2	3.5
$Sn(OH)_2$	5×10^{-26}	—	1.3	2.3	4.3
$Sb(OH)_3$	5×10^{-42}	—	0.2	0.9	2.2

* The experimental pH values refer, strictly speaking, to activity $a = 1$ rather than to the concentration $c = 1$ of the corresponding cations.

** For these hydroxides several values of the solubility product, differing considerably, are given in the literature. Therefore the values given in the table are those giving the closest agreement between the calculated and experimental pH values.

and therefore the OH^- concentration so much that the solubility product of magnesium hydroxide (5×10^{-12}) is not reached. On the other hand, the solubility product of $Fe(OH)_3$ is very much less (3.8×10^{-38}), and this value is greatly exceeded even at the OH^- ion concentration (1.8×10^{-5} g-ion/litre) present in the $NH_4OH + NH_4Cl$ mixture. Therefore $Fe(OH)_3$ is precipitated even in the presence of NH_4Cl.

The difference in the behaviour of Mg^{++} and Fe^{+++} ions with ammonia in the presence of an ammonium salt can be used for separating these ions. Such *separations based on suitable adjustment of the solution* pH are often used in analysis and are of great practical importance.

It was shown above that 0.1 *M* NH_4OH precipitates Mg^{++} in the absence of NH_4Cl. However, as complete precipitation of $Mg(OH)_2$ is achieved at $pH \geqslant 11.3$ while the pH of 0.1 *M* NH_4OH is 11.13, it is clear that the precipitation of Mg^{++} by ammonia cannot be complete. This is especially obvious if we note that one of the products of the reaction

$$MgCl_2 + 2NH_4OH = \downarrow Mg(OH)_2 + 2NH_4Cl$$

is NH_4Cl. Its accumulation in solution gradually lowers the pH, which becomes considerably less than the required value of 11.3 at equilibrium. Accordingly, the precipitation of Mg^{++} by ammonia is very incomplete.

On the other hand, if a strong alkali such as KOH is added instead of NH_4OH to a solution of a magnesium salt, with a small excess it is easy to bring the pH up to 11.3 and thus to achieve practically complete precipitation of the Mg^{++} ion *.

This example shows that, under given conditions, the greater the degree of dissociation of the precipitant used the more complete is the precipitation of the particular ion.

Precipitation of Sparingly Soluble Salts of Weak Acids. The solution pH is also important in the precipitation of various sparingly soluble salts of weak acids, such as carbonates, sulphides, sulphites, phosphates, arsenates, chromates, oxalates, tartrates, etc. The precipitant ions are the anions of the corresponding weak acids, CO_3^{--}, S^{--}, SO_3^{--}, PO_4^{---}, etc. Since these acids are weak (i. e., have a low tendency to dissociate into ions), their anions combine with H^+ ions in solution to give anions such as HCO_3^-, HS^-, HSO_3^-, HPO_4^{--}, $H_2PO_4^-$, etc., and undissociated molecules such as H_2CO_3, H_2S, H_2SO_3, H_3PO_4, etc. Therefore *the concentrations of anions such as* CO_3^{--}, S^{--}, SO_3^{--}, PO_4^{---}, *etc., in solution greatly depend on the* H^+ *ion concentration, decreasing with rise of the latter or with decrease of the solution* pH. Accordingly, the pH also determines whether a given salt is precipitated or not, and the completeness of its precipitation.

As in the case of hydroxides, the pH required for practically complete precipitation of any sparingly soluble salt of a weak acid depends primarily on its solubility product. The lower the solubility product, the less is the concentration of the precipitant ion needed to exceed it. Accordingly, the higher is the H^+ concentra-

* The value pH = 11.3 corresponds to pOH = 2.7. Therefore $\log [OH^-] = -2.7 = \bar{3}.3$ and $[OH^-] = 2 \times 10^{-3}$ g-ion/litre. Since the dissociation of KOH is practically complete and each molecule yields one OH^- ion the excess of KOH in solution must also be 2×10^{-3} *M* (or more) for practically complete precipitation of Mg^{++}. Of course, it is very easy to obtain this excess of alkali in solution.

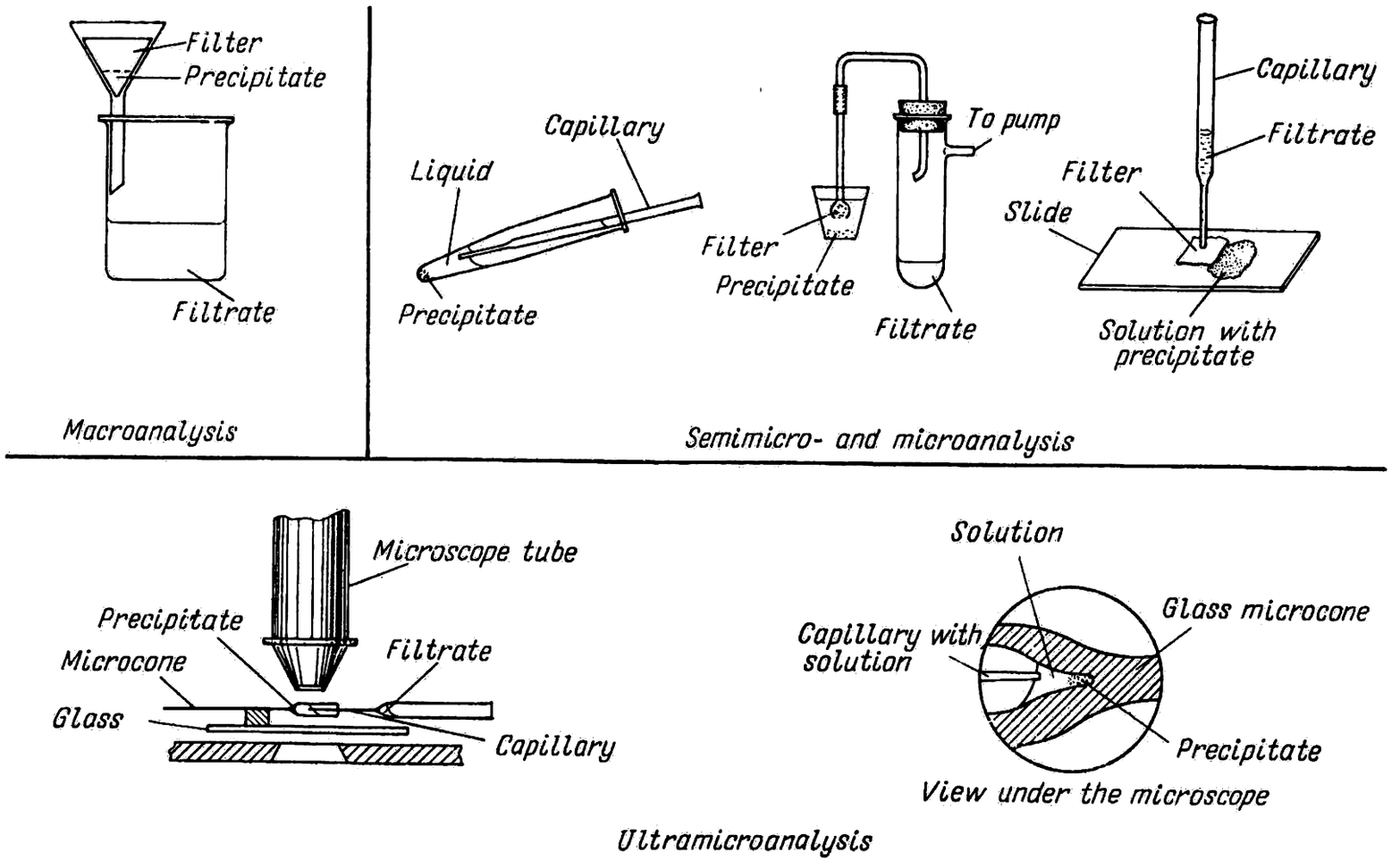


Fig. 1. Separation of precipitate from solution in different methods of analysis

tion (i. e., the lower is the pH) at which the precipitation of the salt is practically complete. For example, the precipitation of cadmium sulphide, CdS ($SP = 3.6 \times 10^{-29}$) by hydrogen sulphide is sufficiently complete even in fairly acid solution ($pH \geqslant 0.5$), whereas manganese sulphide, MnS ($SP = 1.4 \times 10^{-15}$) is precipitated only in alkaline or neutral solution ($pH \geqslant 7$).

In addition to the solubility product, the dissociation constants of the particular weak acids are important. The lower these constants, the greater is the decrease of the concentration of the precipitant ion due to combination with H^+ and the higher the pH required for practically complete precipitation of the salt. For example, as carbonic acid ($K_1 = 4.3 \times 10^{-7}$, $K_2 = 5.6 \times 10^{-11}$) is considerably weaker than oxalic acid ($K_1 = 5.9 \times 10^{-2}$, $K_2 = 6.4 \times \times 10^{-5}$), a higher pH is required to precipitate Ca^{++} as $CaCO_3$ than as CaC_2O_4, although the solubility products of these salts are of the same order of magnitude (4.8×10^{-9} for $CaCO_3$ and 2.6×10^{-9} for CaC_2O_4). This conclusion is fully supported by experiment and calculation. Whereas an alkaline solution ($pH > 9$) is needed for complete precipitation of $CaCO_3$, in the case of CaC_2O_4 the precipitation is complete at $pH \approx 4$.

It is also possible, and generally not very difficult, to calculate the pH required for complete precipitation of any sparingly soluble salt. This matter is discussed in connection with the conditions for precipitation of various sulphides by the action of H_2S (Sec. 39). The precipitants used for sparingly soluble salts of weak acids are generally soluble salts of these acids, which have an alkaline reaction owing to hydrolysis. Therefore in these cases the solution pH is predetermined to a considerable extent by the presence of excess precipitant in solution. The problem here should be faced from another angle; having found the pH produced by the excess of precipitant, we must calculate how completely the particular ion is precipitated at that pH.

As an example, let us examine the precipitation of Group II cations by the group reagent, ammonium carbonate, $(NH_4)_2CO_3$. Being a salt of a weak acid (H_2CO_3) and a weak base (NH_4OH), ammonium carbonate is highly hydrolyzed in aqueous solution*. It is known that the hydrolysis of salts of di- and polybasic acids proceeds by stages. In the present case

the first hydrolysis stage

$$(NH_4)_2CO_3 + H_2O \rightleftarrows NH_4HCO_3 + NH_4OH$$

the second hydrolysis stage

$$NH_4HCO_3 + H_2O \rightleftarrows H_2CO_3 + NH_4OH$$

* The hydrolysis of salts is discussed more fully in Sec. 43.

In ionic form these equations become

$$NH_4^+ + CO_3^{--} + H_2O \rightleftarrows HCO_3^- + NH_4OH$$

$$NH_4^+ + HCO_3^- + H_2O \rightleftarrows H_2CO_3 + NH_4OH$$

It is also known that the lower the degree of dissociation of the hydrolysis products the greater is the extent of hydrolysis. Since the HCO_3^- ion formed at the first stage of hydrolysis is dissociated much less ($K_{HCO_3^-} = K_2 = 5.6 \times 10^{-11}$) than H_2CO_3 ($K_1 = 4.3 \times \times 10^{-7}$), formed in the second stage, the hydrolysis of $(NH_4)_2CO_3$ is incomparably greater at the first stage than at the second. Calculations given later in this book (Sec. 44, Example 2) show that about 90% of all the CO_3^{--} ions are converted into HCO_3^- ions. On the other hand, the second stage of hydrolysis is slight and may be neglected without appreciable error. Therefore we may assume in the first approximation that if in the precipitation of Group II cations the excess of $(NH_4)_2CO_3$ is 0.1 *M*, practically all the CO_3^{--} ions (0.1 g-ion/litre) are converted into HCO_3^- ions, and therefore the concentration of the latter is close to the value $[HCO_3^-] \approx 0.1$ g-ion/litre. On the other hand, the almost complete hydrolysis of $(NH_4)_2CO_3$ at the first stage shows that the solution essentially consists of a mixture of almost equivalent amounts of free ammonia and an ammonium salt (NH_4HCO_3), and *is therefore an ammonium buffer mixture with* pH $\approx$ 9.2. This pH value corresponds to $[H^+] \approx 6 \times 10^{-10}$ g-ion/litre. Substituting the values found for $[HCO_3^-]$ and $[H^+]$ into the equation for K_2 of carbonic acid, we have

$$K_2 = \frac{[H^+] \cdot [CO_3^{--}]}{[HCO_3^-]} = \frac{6 \times 10^{-10} [CO_3^{--}]}{10^{-1}} = 5.6 \times 10^{-11}$$

and hence

$$[CO_3^{--}] = \frac{5.6 \times 10^{-11} \times 10^{-1}}{6 \times 10^{-10}} \approx 10^{-2}$$

More precise calculations with the incompleteness of hydrolysis taken into account give similar values: $[CO_3^{--}] = 1.4 \times 10^{-2}$ g-ion/litre and pH = 9.13 (Sec. 44, Example 2). Knowing the CO_3^{--} concentration, we can easily find the concentrations of the metal ions in solution at the end of precipitation from the solubility products of the carbonates. For example:

$$[Ba^{++}] = \frac{SP_{BaCO_3}}{[CO_3^{--}]} = \frac{8 \times 10^{-9}}{1.4 \times 10^{-2}} = 5.7 \times 10^{-7} \text{ g-ion/litre}$$

Therefore the precipitation of Ba^{++} is practically complete. Since the solubility products of $CaCO_3$ (4.8×10^{-9}) and $SrCO_3$

(1.6×10^{-9}) are even less than that of $BaCO_3$, Ca^{++} and Sr^{++} are precipitated even more completely at the given pH.

Precipitation of Sparingly Soluble Salts of Strong Acids. Sparingly soluble salts of strong monobasic acids, such as AgCl, AgBr, AgI, etc., are precipitated by their anions: Cl^-, Br^-, I^-, etc. These anions evidently cannot combine with H^+ ions because HCl, HBr and HI are almost completely dissociated in solution. Therefore the completeness of precipitation of their silver salts is almost independent of the solution pH. Sometimes the influence of excess acid in solution has to be taken into account, but this is only because the salt effect increases or the cations of the precipitated salts combine with the acid anions to give complexes, raising the solubility of the precipitate.

The situation is somewhat different in the case of sparingly soluble sulphates, as the dissociation of H_2SO_4 is almost complete only at the first stage, i. e., with formation of H^+ and HSO_4^- ions. Although the second dissociation stage

$$HSO_4^- \rightleftarrows H^+ + SO_4^{--}$$

is considerable ($K_2 = 1.2 \times 10^{-2}$), it is not complete. Therefore at not too low SO_4^{--} concentrations and sufficiently high H^+ ion concentrations these ions partially combine to form HSO_4^- anions. Accordingly, the solution pH is not entirely immaterial in this case. The precipitation of sparingly soluble sulphates should be rather less complete in strongly acid solutions than in neutral and alkaline solutions. In the practice of qualitative analysis this has to be taken into consideration only in the precipitation of the more soluble sulphates, $CaSO_4$, $SrSO_4$ and $PbSO_4$. The least soluble of the sulphates, $BaSO_4$, is precipitated completely even from strongly acid solutions.

Regulation of the Solution pH. It was shown above that suitable regulation of the solution pH is usually needed for satisfactory separation of ions. This is effected by addition of suitable acids, alkalies or buffer mixtures to the unknown solution. The acid or alkali is added drop by drop, the solution being stirred continuously and tested with the appropriate indicator papers or with universal indicator. Sometimes the indicator is added to the solution and the addition of acid or alkali is continued until one drop produces a colour change.

In choosing the acid or alkali one must be sure that the ions introduced with it do not interfere with detection of any ions in the unknown solution and do not cause any complications in the subsequent analysis. For example, when K^+ is to be detected, acid solutions must not be neutralized with KOH or NH_4OH; it is imperative to use NaOH. Conversely, for detection of Na^+ use is made

of rather KOH than NaOH for neutralization. In the same way, sulphuric acid should not be used for neutralizing alkaline solutions which may contain Group II cations or Pb^{++}, as it precipitates the sparingly soluble sulphates of these cations, thereby complicating the analysis. In many cases, it is not sufficient to adjust the pH to the required value before precipitation; it must be remembered that the pH may alter as the result of the precipitation reaction. This occurs when sparingly soluble salts are precipitated by the corresponding free acids:

$$K^+ + H_2C_4H_4O_6 \rightleftarrows \downarrow KHC_4H_4O_6 + H^+$$

$$Ca^{++} + H_2C_2O_4 \rightleftarrows \downarrow CaC_2O_4 + 2H^+$$

$$Zn^{++} + H_2S \rightleftarrows \downarrow ZnS + 2H^+$$

The above equations show that H^+ ions are produced by these reactions, so that the pH gradually falls as the precipitation proceeds. Therefore the precipitation is incomplete if appropriate steps are not taken to prevent this fall of pH. Various buffer mixtures are able to resist changes of solution pH. Therefore a suitable buffer mixture must be added to regulate the pH. For example, the first two of the above reactions are carried out in the presence of acetate buffer mixture with pH $\approx$ 4.7, when K^+ and Ca^{++} are precipitated practically completely because the H^+ ions are combined with the CH_3COO^- anions from sodium acetate. Similarly, Zn^{++} can be precipitated by hydrogen sulphide in the presence of formate buffer mixture (formic acid, HCOOH, and a formate salt) with pH $\approx$ 2, when zinc sulphide is precipitated almost completely while precipitation of other sulphides of Group III cations is prevented. This procedure can be used for fractional detection of Zn^{++} in the presence of all the other Group III cations.

The use of buffer mixtures is also convenient because they provide a definite pH despite the presence of small amounts of acid or alkali before the addition. It should be remembered, however, that every buffer mixture has a definite buffer capacity and can combine with a definite but not too large an amount of H^+ or OH^- ions. If either of these ions should be present in very large excess, the pH would be far from the expected value and would not remain constant (see p. 77).

It follows that in strongly acid or strongly alkaline solutions either most of the acid or alkali must be previously neutralized before addition of the buffer mixture, or a buffer mixture having a sufficiently high buffer capacity, i.e., with high enough concentrations of both components must be used. Only then would the buffer mixture be effective.

27. Fractional Precipitation

It often happens in analytical practice that the reagent used forms sparingly soluble electrolytes not with one but with two or more of the ions present. For example, this occurs when group reagents are used. How does precipitation proceed in such cases? This question is easily settled with the aid of the solubility product rule.

Suppose, for example, that we have a mixture of KCl and K_2CrO_4 solutions such that $[Cl^-] = [CrO_4^{--}] = 1 \times 10^{-1}$ g-ion/litre. We add $AgNO_3$ solution to this mixture drop by drop. The Cl^- and CrO_4^{--} ions then meet Ag^+ ions and the following reactions become possible:

$$Ag^+ + Cl^- = \downarrow AgCl$$

$$2Ag^+ + CrO_4^{--} = \downarrow Ag_2CrO_4$$

Which of the two salts is precipitated first? Evidently *the one whose solubility product is reached first* (*i.e., at a lower concentration of* Ag^+). The Ag^+ concentrations needed to start the precipitation of AgCl and Ag_2CrO_4 at the given Cl^- and CrO_4^{--} concentrations are easily calculated from their solubility products (see Table IV, Appendix):

$$[Ag^+] \cdot [Cl^-] = SP_{AgCl} = 1.56 \times 10^{-10}$$

$$[Ag^+]^2 \cdot [CrO_4^{--}] = SP_{Ag_2CrO_4} = 9 \times 10^{-12}$$

Denoting these concentrations by $[Ag^+]_{AgCl}$ and $[Ag^+]_{Ag_2CrO_4}$, respectively, we can write:

$$[Ag^+]_{AgCl} = \frac{SP_{AgCl}}{[Cl^-]} = \frac{1.56 \times 10^{-10}}{1 \times 10^{-1}} = 1.56 \times 10^{-9} \text{ g-ion/litre}$$

$$[Ag^+]_{Ag_2CrO_4} = \sqrt{\frac{SP_{Ag_2CrO_4}}{[CrO_4^{--}]}} = \sqrt{\frac{9 \times 10^{-12}}{1 \times 10^{-1}}} = 9.5 \times 10^{-6} \text{ g-ion/litre}$$

Therefore AgCl is precipitated first; it is the less soluble salt* and its solubility product is reached earlier than that of Ag_2CrO_4.

This is easy to confirm by experiment. Mix a few drops of KCl and K_2CrO_4 solutions of the same molar concentration in a small test tube and add $AgNO_3$ solution to the mixture drop by drop, mixing the contents of the tube thoroughly after each addition. First a white curdy precipitate of AgCl is formed, followed by a brick-red Ag_2CrO_4 precipitate.

When does the precipitation of the second salt begin? This is also easy to calculate with the aid of the solubility product rule. The product $[Ag^+] \cdot [Cl^-]$ of the ion concentrations remains constant

---

* See Sec. 24, Examples 1 and 2 for the solubilities of AgCl and Ag_2CrO_4.

throughout the precipitation and is equal to the solubility product of AgCl. Therefore the Ag^+ ion concentration in solution must gradually rise as the Cl^- ions are precipitated. Ultimately it reaches the level needed for precipitation of CrO_4^{--} ions and both salts are then precipitated together (in relative amounts determined by the ratio of their concentrations in solution at that instant). This occurs when

$$\frac{SP_{AgCl}}{[Cl^-]} = \sqrt{\frac{SP_{Ag_2CrO_4}}{[CrO_4^{--}]}}$$

Rearranging this expression, we have

$$\frac{\sqrt{[CrO_4^{--}]}}{[Cl^-]} = \frac{\sqrt{SP_{Ag_2CrO_4}}}{SP_{AgCl}} = \frac{\sqrt{9 \times 10^{-12}}}{1.56 \times 10^{-10}} \approx 2 \times 10^4$$

The CrO_4^{--} ion concentration in solution is known to be 1×10^{-1} g-ion/litre. From this it is easy to find the Cl^- concentration at that instant:

or

$$\frac{\sqrt{1 \times 10^{-1}}}{[Cl^-]} \approx 2 \times 10^4$$

$$[Cl^-] \approx \frac{0.32}{2 \times 10^4} = 1.6 \times 10^{-5} \text{ g-ion/litre}$$

Therefore precipitation of CrO_4^{--} begins only after the Cl^- ions have been almost completely removed from solution. From this it follows that *ions are precipitated consecutively from a mixture containing them and individual sparingly soluble electrolytes are precipitated in the sequence in which their solubility products are reached as the concentration of the precipitant ions is raised.*

When the initial concentrations of the precipitated ions are different, the sequence of their precipitation evidently depends also on their concentrations, and may be reversed by suitable adjustment of the latter. For example, if the Cl^- and CrO_4^{--} concentrations are so chosen that

$$\frac{\sqrt{[CrO_4^{--}]}}{[Cl^-]} > \frac{\sqrt{SP_{Ag_2CrO_4}}}{SP_{AgCl}}$$

the first to be precipitated will be Ag_2CrO_4 and not AgCl.

28. Dissolution of Precipitates

The above examples show how the solubility product rule is used for solving various problems associated with the precipitation of ions in the form of sparingly soluble electrolytes. It is no less useful for solving the reverse problem, equally important in analy-

sis—to find the conditions for dissolving sparingly soluble precipitates.

Suppose that we want to dissolve a precipitate of $Mg(OH)_2$ [for example, in order to detect Mg^{++} in the resultant solution and to confirm that the precipitate was in fact $Mg(OH)_2$]. We first note that the solution in contact with this precipitate is saturated with $Mg(OH)_2$. This means that the ionic product $[Mg^{++}] \cdot [OH^-]^2$ is equal to the solubility product of $Mg(OH)_2$, namely 5×10^{-12} (at 25°).

What happens if a small amount of acid is added to this solution? The hydrogen ions of the acid combine with the hydroxyl ions present in solution (formed by dissociation of magnesium hydroxide) to give undissociated H_2O molecules, and as a result the ionic product $[Mg^{++}] \cdot [OH^-]^2$ becomes less than the solubility product of $Mg(OH)_2$. The solution then becomes unsaturated with magnesium hydroxide and begins to dissolve the precipitate of this substance in contact with it. This evidently continues until the ionic product $[Mg^{++}] \cdot [OH^-]^2$ has again reached the solubility product of $Mg(OH)_2$, and equilibrium then becomes established. If the addition of acid is continued, this equilibrium is continuously disturbed and additional amounts of the precipitate dissolve. Finally the whole precipitate dissolves.

We therefore see that *in order to dissolve a precipitate of a sparingly soluble electrolyte we must bind one of the ions which it yields. This is effected by the addition of an electrolyte the ions of which can form, with one of the ions of the sparingly soluble electrolyte, a compound with a low degree of dissociation.*

The reaction which takes place when acids act on $Mg(OH)_2$ can be represented by the following ionic equation:

$$Mg(OH)_2 + 2H^+ = Mg^{++} + 2H_2O$$

Other sparingly soluble compounds dissolve in acids similarly, for example:

$$Mn(OH)_2 + 2H^+ = Mn^{++} + 2H_2O$$
$$Fe(OH)_3 + 3H^+ = Fe^{+++} + 3H_2O$$

It is also possible to bind OH^- ions in another way, by introducing NH_4^+ ions into the solution, when the compound NH_4OH is formed. The degree of dissociation of this compound is relatively low. Therefore many hydroxides dissolve not only in acids but also in ammonium salts, for example:

$$Mg(OH)_2 + 2NH_4^+ = Mg^{++} + 2NH_4OH$$
$$Mn(OH)_2 + 2NH_4^+ = Mn^{++} + 2NH_4OH$$

However, as NH_4OH is dissociated much more than H_2O the decrease of the OH^- ion concentration is not as great as when an acid

is added. Therefore ammonium salts should have a much weaker solvent effect than acids on hydroxides. This is found to be so; only the more soluble bases dissolve in ammonium salts. The less soluble bases, such as $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, etc., which dissolve readily in acids, are insoluble in ammonium salts.

Acids sparingly soluble in water can, evidently, be dissolved if the H^+ ions in solution are made to combine with OH^- ions (by additions of an alkali); for example:

$$H_2WO_4 + 2OH^- = WO_4^{--} + 2H_2O$$

Sparingly soluble salts of weak acids should dissolve in acids because the H^+ ions of the acid combine with the salt anions to give undissociated molecules of the corresponding weak acid, for example:

$$KHC_4H_4O_6 + H^+ = H_2C_4H_4O_6 + K^+$$

Here the $HC_4H_4O_6^-$ anions released into the solution from the precipitate combine with H^+ ions to give molecules of tartaric acid, $H_2C_4H_4O_6$, which is dissociated to only a slight extent. As the concentration of these anions decreases the K^+ ion concentration in solution must increase because of the dissolution of the $KHC_4H_4O_6$ precipitate. Similarly, a CaC_2O_4 precipitate dissolves in acids as the result of the reactions:

$$CaC_2O_4 + H^+ = Ca^{++} + HC_2O_4^-$$
$$HC_2O_4^- + H^+ = H_2C_2O_4$$

Sulphides which are sparingly soluble in water can be dissolved similarly, for example:

$$ZnS + H^+ = Zn^{++} + HS^-$$
$$HS^- + H^+ = H_2S \uparrow$$

On the other hand, *sparingly soluble salts of strong acids*, such as $BaSO_4$, $SrSO_4$, AgCl, AgI, etc., *do not dissolve in acids* because no compounds of a low degree of dissociation can form in this case*.

We must also consider the dissolution of precipitates consisting of acid salts. It is known that salts such as $KHC_4H_4O_6$ dissolve in alkalies as well as in acids. This is because the $HC_4H_4O_6^-$ ions in solution, derived from the $KHC_4H_4O_6$ precipitate, partially dissociate:

$$HC_4H_4O_6^- \rightleftarrows H^+ + C_4H_4O_6^{--}$$

The OH^- ions introduced with the alkali combine with the H^+ ions formed as the result of this dissociation, and as a result of this

---

* It should be noted, however, that sparingly soluble sulphates are somewhat more soluble in acids because SO_4^{--} ions combine with H^+ ions of the acids to give HSO_4^- anions (see p. 132).

the equilibrium is shifted to the right, and the $HC_4H_4O_6^-$ ion concentration falls. Therefore the K^+ ion concentration increases and the precipitate dissolves if enough alkali is present. The ionic equation of this reaction is

$$KHC_4H_4O_6 + OH^- = K^+ + C_4H_4O_6^{--} + H_2O$$

In all the cases considered above the formation of undissociated molecules of a weak electrolyte (water, weak acids, NH_4OH, etc.) is the reason why ions are removed during dissolution of precipitates.

However, ions can also be bound or removed *by formation of sufficiently stable complex compounds.* Therefore very often the dissolution of precipitates is due to the formation of complex compounds*. For example, although silver chloride is almost insoluble in acids it dissolves very easily in NH_4OH. This is because the Ag^+ ions in solution, yielded by the precipitate, form complex $[Ag(NH_3)_2]^+$ ions with NH_3 molecules (which are always present in solution because the reaction between NH_3 and H_2O is reversible). The resultant lowering of the Ag^+ ion concentration in solution disturbs the equilibrium between the solution and the precipitate, and the latter dissolves.

The ionic equation of this reaction is

$$AgCl + 2NH_3 = [Ag(NH_3)_2]^+ + Cl^-$$

In the same way, HgI_2 dissolves readily in KI because its Hg^{++} ions form complex HgI_4^{--} ions with the I^- ions formed by dissociation of KI:

$$HgI_2 + 2KI = K_2[HgI_4]$$

or

$$HgI_2 + 2I^- = [HgI_4]^{--}$$

This example shows that in this case the solubility of the HgI_2 precipitate is not lowered by the introduction of the common ion I^-; on the contrary, the precipitate dissolves completely.

It has already been pointed out that one reason why a large excess of precipitant should not be added for separation reactions is the possible formation of complex compounds.

Finally, the dissolution of precipitates is very often associated with various oxidation-reduction processes. For example, sulphides

---

* Complex compounds, with which the student is already familiar from the course of general chemistry, are considered in Sections 46 to 49. It will be remembered that although the complex ions in these compounds, such as $[Ag(NH_3)_2]^+$ can dissociate to yield the corresponding simple ions (Ag^+), the degree of this dissociation is usually very low. Therefore the formation of such complex ions has an influence similar to that of the formation of undissociated molecules of weak electrolytes on the dissolution of precipitates.

such as CoS, NiS, CuS, Bi_2S_3, etc., which are insoluble in other acids, dissolve readily when heated with concentrated HNO_3. In the case of CuS the reaction is

$$3CuS + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + \downarrow 3S + 2NO \uparrow$$

The reaction consists essentially of the oxidation of the S^{--} ions, yielded in solution by the precipitate, to free sulphur by nitric acid. As a result the S^{--} ion concentration falls and the Cu^{++} concentration rises, i.e., the CuS precipitate dissolves.

It often happens that a precipitate insoluble in HCl can be dissolved in HNO_3. Therefore when a substance sparingly soluble in water is to be dissolved, the effect of HCl is tried first. If the precipitate does not dissolve in hydrochloric acid, it is tested with concentrated HNO_3 and finally with aqua regia (a mixture of 1 volume of concentrated HNO_3 with 3 volumes of concentrated HCl), which is an even stronger oxidizing agent than nitric acid.

Sometimes it is necessary to reduce one of its constituent ions in order to dissolve a precipitate. For example, the hydroxide of quadrivalent manganese, $MnO(OH)_2$, is insoluble in H_2SO_4, but if KNO_2 or $NaNO_2$ is also added Mn^{+IV} is reduced to Mn^{+II} and the precipitate dissolves*. The equation of this reaction is

$$MnO(OH)_2 + KNO_2 + H_2SO_4 = MnSO_4 + KNO_3 + 2H_2O$$

Of course, there is no point in using oxidizing (or reducing) agents unless one of the ions can be oxidized (or reduced).

It would obviously be quite useless to try to dissolve $BaSO_4$, in which the elements Ba and S are in their highest valency states and cannot be oxidized in HNO_3 or aqua regia.

Some additional information on the dissolution process is given in Sections 40 and 112.

29. Interconversion of Sparingly Soluble Electrolytes

Reactions in which one sparingly soluble electrolyte, such as Ag_2CrO_4, is converted into another, such as AgCl, by the action of a suitable reagent (KCl), are very closely related to the dissolution processes discussed above.

The cause of such reactions is not difficult to understand. The solution over the Ag_2CrO_4 precipitate contains Ag^+ ions, which meet Cl^- ions when KCl is added. As AgCl is less soluble than Ag_2CrO_4, the Ag^+ concentration is sufficient to exceed the solubility product of silver chloride, and the latter is precipitated. However, the removal of Ag^+ ions makes the solution unsaturated with respect

* The Roman numerals indicate the valency of the element.

to Ag_2CrO_4, which therefore dissolves. The resulting Ag^+ ions again combine at once with Cl^- ions, etc. These processes, schematically represented as

$$\begin{array}{c} Ag_2CrO_4 \rightleftarrows 2Ag^+ + CrO_4^{--} \\ + \\ 2KCl \longrightarrow 2Cl^- + 2K^+ \\ \downarrow \\ 2AgCl \\ \text{Precipitate} \end{array}$$

lead to complete conversion of Ag_2CrO_4 into AgCl if enough KCl is present.

This can be easily demonstrated by experiment. Add $AgNO_3$ solution to a few drops of K_2CrO_4 solution. A precipitate of Ag_2CrO_4 is formed; add an excess of KCl solution and shake the test tube. The red precipitate (Ag_2CrO_4) turns white (AgCl).

In the same way, it is easy to convert various other sparingly soluble compounds into compounds of even lower solubility. For example, $SrSO_4$ ($SP = 2.8 \times 10^{-7}$) is readily converted into $SrCO_3$ ($SP = 1.6 \times 10^{-9}$) by the action of Na_2CO_3 solution.

This is of great practical importance, as $SrSO_4$, being a sparingly soluble salt of a strong acid, is insoluble in acids (Sec. 28). Therefore to dissolve strontium sulphate it is first converted into the carbonate, which is a salt soluble in acids.

Comparison of the solubility products of $BaSO_4$ (1.1×10^{-10}) and $BaCO_3$ (8×10^{-9}) might suggest that barium sulphate cannot be converted into the carbonate in this way. However, this is not the case. $BaCO_3$ is always precipitated when its solubility product is exceeded, i.e., when

$$[Ba^{++}] \cdot [CO_3^{--}] > SP_{BaCO_3}$$

or

$$[Ba^{++}] > \frac{SP_{BaCO_3}}{[CO_3^{--}]}$$

However, in this case the Ba^{++} concentration is determined by the solubility of $BaSO_4$, and is given by the expression

$$[Ba^{++}] = \frac{SP_{BaSO_4}}{[SO_4^{--}]}$$

Comparing this with the inequality given above, we find that $BaSO_4$ would be converted into $BaCO_3$ under the condition that

$$\frac{SP_{BaSO_4}}{[SO_4^{--}]} > \frac{SP_{BaCO_3}}{[CO_3^{--}]}$$

i.e., if

$$\frac{[CO_3^{--}]}{[SO_4^{--}]} > \frac{SP_{BaCO_3}}{SP_{BaSO_4}}$$

Substituting the numerical values of the solubility products into this expression, we have

$$\frac{[CO_3^{--}]}{[SO_4^{--}]} > \frac{8 \times 10^{-9}}{1.1 \times 10^{-10}} \text{ or } \frac{[CO_3^{--}]}{[SO_4^{--}]} > 73$$

Therefore for conversion of $BaSO_4$ into $BaCO_3$ to occur the CO_3^{--} concentration in solution must be more than 73 times the SO_4^{--} concentration. As the latter is very low (about 1×10^{-5} g-ion/litre), this condition is easily satisfied.

However, it is easy to see that the reaction does not go to completion. From the equation

$$BaSO_4 + CO_3^{--} \rightleftarrows BaCO_3 + SO_4^{--}$$

it is clear that as the reaction proceeds the CO_3^{--} concentration falls while the SO_4^{--} concentration rises. As soon as the ratio of these concentrations becomes equal to 73 equilibrium is established and further conversion of $BaSO_4$ into $BaCO_3$ ceases.

However, if we decant the liquid from the precipitate and act on the latter with a fresh portion of carbonate solution the reaction begins again. By repeating this operation several times we can achieve complete conversion of $BaSO_4$ into $BaCO_3$.

Thus, although it is possible to convert $BaSO_4$ into the more soluble compound $BaCO_3$, the reaction proceeds with difficulty and does not go to completion in a single treatment with the reagent (Na_2CO_3). It is not difficult to see that the possibility of conversion is itself based on the fact that the solubility products of the sulphate and carbonate do not differ very greatly (by a factor of 73).

On the other hand, in the reaction

$$AgI + Cl^- \rightleftarrows AgCl + I^-$$

the solubility product of the compound formed (AgCl) is about 1,000,000 times the solubility product of the original compound (AgI). This reaction does not occur to any appreciable extent, even on repeated treatment of AgI with KCl solution. In contrast, the reverse reaction—conversion of AgCl into AgI—proceeds very easily and is practically complete even after a single treatment of AgCl with KI solution. This is easily shown by experiment. If we precipitate AgCl, separate it from the mother liquor, and shake it with KI solution, the precipitate turns yellow because of the conversion of AgCl into AgI.

Interconversion of sparingly soluble compounds can be used for ion separation, and especially in fractional detection of ions. Solid sparingly soluble reagents sometimes have considerable advantages as precipitants over readily soluble compounds because of their higher selectivity. For example, if we add a soluble cadmium salt such as $CdSO_4$, to a solution containing S^{--} and SO_3^{--} ions, both these ions are precipitated because their cadmium salts are sparingly soluble. If we replace $CdSO_4$ by the sparingly soluble $CdCO_3$, which is more soluble than CdS but less so than $CdSO_3$, we precipitate S^{--} but not SO_3^{--}.

In the same way it is possible to separate Cu^{++} from Cd^{++} ions in sulphate solution by the action of solid PbS. The following reactions occur

$$PbS + Cu^{++} = \downarrow CuS + Pb^{++}$$

$$Pb^{++} + SO_4^{--} = \downarrow PbSO_4$$

The Cd^{++} ions remain in solution and are thus separated from the Cu^{++} ions. If H_2S was used, the sulphides of both metals would be precipitated.

Reactions involving the conversion of a sparingly soluble compound into another, even less soluble under the given conditions, can also be used for separating ions by another method. It is sometimes possible to dissolve out only one kind of ion from a mixture of several sparingly soluble substances by the action of a suitable reagent; it is thereby separated from the others and can be detected in the solution by suitable tests.

For example, the anion of thiocyanic acid (HCNS) is detected by the action of $FeCl_3$, with which it forms the intensely red ferric thiocyanate, $Fe(CNS)_3$:

$$3CNS^- + Fe^{+++} \rightleftarrows Fe(CNS)_3$$

The presence of I^- ions interferes with this reaction, as they are oxidized by Fe^{+++} to free iodine, which also produces a red-brown colour similar to that of $Fe(CNS)_3$:

$$2I^- + 2Fe^{+++} = I_2 + 2Fe^{++}$$

The separation of I^- from CNS^- ions may be effected as follows. The solution is acidified with HNO_3 and $AgNO_3$ solution is added. This precipitates I^- and CNS^- as AgI and AgCNS. The precipitate is separated from the solution, washed, and shaken with excess KBr. As the solubility product of AgBr (7.7×10^{-13}) is less than that of AgCNS (1.16×10^{-12}), silver thiocyanate is converted into the silver bromide:

$$AgCNS + Br^- = AgBr + CNS^-$$

The CNS^- ions in solution can be detected by the reaction with $FeCl_3$. Since the solubility product of AgI (1.5×10^{-16}) is much less than that of AgBr, the action of KBr does not convert AgI into AgBr to any appreciable extent, and therefore I^- ions do not pass into solution. Consequently, there is no interference by I^- in the detection of CNS^-.

The choice of the reagent for separating only one kind of ion from a precipitate can be based on a comparison of the solubility products of the corresponding compounds only if the formulas of the precipitates formed are all of the same type, as in the preceding example. In the case of precipitates with formulas of different types, such as $Ag_4[Fe(CN)_6]$ and AgBr, or AgI and Ag_2S, etc., the so-called *reduced solubility products* must be used when the choice is made. For example, in the case of the reaction

$$Ag_4[Fe(CN)_6] + 4Br^- \rightleftarrows 4AgBr + [Fe(CN)_6]^{=}$$

the equilibrium constant

$$K = \frac{[Fe(CN)_6]^{=}}{[Br^-]^4} = \frac{SP_{Ag_4[Fe(CN)_6]}}{(SP_{AgBr})^4} = \frac{1.5 \times 10^{-41}}{(7.7 \times 10^{-13})^4} = \frac{1.5 \times 10^{-41}}{3.5 \times 10^{-49}} = 4.3 \times 10^7$$

depends on the fourth and not the first power of SP_{AgBr}. This fourth power value (3.5×10^{-49}) is known, in N. A. Tananaev's terminology, as the reduced solubility product of silver bromide. It is equal to the solubility product of the substance (AgBr) raised to the appropriate power as indicated by the coefficient in the reaction equation.

The fact that the equilibrium constant of this reaction is very large (4.3×10^7) shows that at equilibrium the concentration of the reaction products, $[Fe(CN)_6]^{=}$ ions, is very much higher than the concentration of the residual Br^- ions. This means that *the reaction equilibrium is shifted strongly to the right, towards formation of the substance* (AgBr) *with the smaller reduced solubility product.*

If we arrange various silver salts in the order of decreasing reduced solubility products, we obtain the following series*:

$Ag_3[Fe(CN)_6]$	$\longrightarrow$	AgCl	$\longrightarrow$	$Ag_4[Fe(CN)_6]$	$\longrightarrow$	AgCN	$\longrightarrow$
$(9.8 \times 10^{-26})^{4/3}$		$(1.56 \times 10^{-10})^4$		1.5×10^{-41}		$(2 \times 10^{-12})^4$	
4.5×10^{-34}		5.9×10^{-40}		1.5×10^{-41}		1.6×10^{-47}	

$\longrightarrow$	AgCNS	$\longrightarrow$	AgBr	$\longrightarrow$	AgI	$\longrightarrow$	Ag_2S
	$(1.16 \times 10^{-12})^4$		$(7.7 \times 10^{-13})^4$		$(1.5 \times 10^{-16})^4$		$(1.6 \times 10^{-49})^2$
	1.8×10^{-48}		3.5×10^{-49}		5.1×10^{-64}		3.6×10^{-98}

It was shown above that the interconversion of sparingly soluble compounds proceeds predominantly towards formation of compounds with smaller reduced solubility products. Therefore if we act with KI solution on the precipitates of all the silver salts in the above series, those to the left of AgI are converted into silver iodide, and the corresponding anions, i.e., $[Fe(CN)_6]^{---}$, Cl^-, $[Fe(CN)_6]^{=}$, CNS^- and Br^-, pass into solution. On the other hand, Ag_2S,

* The numerical values of the reduced solubility products are given in the bottom line of the series. The middle line indicates the method of calculation.

which is to the right of AgI in the series and has a smaller reduced solubility product, is not converted into silver iodide to any appreciable extent by the action of KI, and no noticeable amounts of S^{--} ions pass into solution.

However, this rule is completely valid only if the differences between the reduced solubility products are sufficiently large. For example, both bromide and chloride solutions dissolve out appreciable amounts of CNS^- ions from an AgCNS precipitate, although silver chloride has a smaller reduced solubility product than silver thiocyanate.

Similar series may be formed for other sparingly soluble compounds, such as barium and lead salts, sulphides of various metals, etc.

These examples illustrate the nature and significance of N. A. Tananaev's *series rule.*

30. Direction of Exchange Reactions

One of the most important factors determining the direction of an exchange reaction is evidently the low solubility of one of the reaction products. If one of the electrolytes formed in a reaction has a low solubility product, its value is greatly exceeded and the reaction proceeds towards practically complete precipitation of this electrolyte. If more than one sparingly soluble electrolyte can be formed in a reaction, the least soluble is usually precipitated first, etc.

Another factor determining the direction of exchange reactions is the formation of compounds of a low degree of dissociation; this point was considered in relation to the dissolution of precipitates. Reactions of this type also include neutralization, which consists essentially of the combination of H^+ and OH^- ions:

$$H^+ + OH^- = H_2O$$

Displacement of weak acids from their salts by strong acids, or of weak bases by strong alkalies, is another consequence of the formation of substances of a low degree of dissociation. For example, if HCl solution is added to a solution of sodium acetate, CH_3COONa, most of the H^+ ions of the acid immediately combine with CH_3COO^- ions to form undissociated molecules of the weak acetic acid:

$$CH_3COONa + HCl = CH_3COOH + NaCl$$

or

$$CH_3COO^- + H^+ = CH_3COOH$$

The solution becomes appreciably less acid.

It was shown earlier that this is often used in practice to decrease solution acidity in reactions involving the formation of precipitates soluble in strong acids but insoluble in acetic acid (such as $KHC_4H_4O_6$, CaC_2O_4, $BaCrO_4$, ZnS, etc.). The reactions are carried out in the presence of sodium acetate. If this is taken somewhat in excess, an acetate buffer mixture is formed, and this maintains the pH almost constant at a value permitting the complete precipitation of these salts.

Sometimes reactions between strong acids and salts of weak acids are used for neutralization of acid solutions; generally carbonates such as Na_2CO_3, K_2CO_3, $CaCO_3$, etc., are used. Free H_2CO_3 is formed, which decomposes into its anhydride and water:

$$2HCl + CaCO_3 = CaCl_2 + \uparrow CO_2 + H_2O$$

or

$$2H^+ + CaCO_3 = Ca^{++} + \uparrow CO_2 + H_2O$$

A strong alkali can also be replaced by the weak base NH_4OH by the action of an ammonium salt on the solution, for example:

$$NaOH + NH_4Cl = NaCl + NH_4OH$$

or

$$OH^- + NH_4^+ = NH_4OH$$

The decrease in the concentrations of particular ions, needed for exchange reactions to proceed, may occur not only as the result of formation of compounds of low solubility or degree of dissociation, but also owing to formation of a compound which is volatile under the given conditions. For example if the reaction

$$NaCl + H_2SO_4 = NaHSO_4 + HCl \uparrow$$

is carried out with heating or in the absence of water, HCl is removed in the form of a gas.

Similarly, when nitrate solutions are evaporated with H_2SO_4, sulphuric acid displaces free HNO_3 which escapes in vapour form; for example:

$$Cu(NO_3)_2 + H_2SO_4 = CuSO_4 + 2HNO_3 \uparrow$$

This method is used for removing NO_3^- ions whenever their presence in solution is undesirable (because of their oxidizing action).

It is evident that *in order to obtain any acid from one of its salts by this method the salt must be treated with an acid which is less volatile than the one formed.* Sulphuric acid is generally used as a relatively non-volatile acid.

By taking advantage of differences in volatility, we can sometimes displace a stronger acid from one of its salts by a weaker one. For example, when sodium chloride, NaCl, is evaporated with boric acid, H_3BO_3, which is one of the weakest acids, the latter, being non-volatile, displaces HCl from the salt. An analogous case, dependent on the low solubility of one of the reaction products, is the reaction

$$CuCl_2 + H_2S = \downarrow CuS + 2HCl$$

From all this it follows that *a necessary condition for the occurrence of exchange reactions in electrolyte solutions is the removal*

of particular ions from solution as the result of low solubility, volatility, or low degree of dissociation of one of the reaction products.

If no compounds with such properties can be formed, the reaction does not occur.

This becomes very clear if we attempt to write the ionic equation for such a reaction, for example

$$NaCl + KNO_3 = NaNO_3 + KCl$$

We find that all the terms in the two sides of the ionic equation are exactly the same, and therefore cancel out:

$$Na^+ + Cl^- + K^+ + NO_3^- = Na^+ + NO_3^- + K^+ + Cl^-$$

This obviously means that no reaction takes place in the solution.

31. Modern Views on the Nature of Acids and Bases

We saw earlier that when a salt of a weak acid acts on a solution of a strong acid the acidity of the solution decreases greatly. In some instances the acid may be completely neutralized, as by an alkali. In practice acid solutions are often neutralized by sodium carbonate, Na_2CO_3, which reacts with acids as follows:

$$2H^+ + CO_3^{--} = H_2CO_3 = H_2O + CO_2 \uparrow$$

Analogous effects are also observed when strong bases react with salts of weak bases. These reactions evidently have much in common with neutralization reactions, as they lead to a decrease or total disappearance of the acidic or alkaline properties of solutions. Yet no indication at all of this similarity is given by the theory of electrolytic dissociation, according to which neutralization is regarded entirely as a process of combination of H^+ ions with OH^- ions, leading to the formation of undissociated water molecules. This concept of neutralization is undoubtedly too narrow.

Another defect of the usual views on acids and bases, derived from the theory of electrolytic dissociation, is that they are applicable only to aqueous solutions, and not to solutions in other solvents. This is shown by the following examples. We are accustomed to regarding ammonium chloride as a typical salt by its behaviour in aqueous solutions; but when dissolved in liquid ammonia it behaves as a strong acid and exhibits all the typical properties of acids, up to the ability to dissolve metals with evolution of hydrogen, although these solutions evidently cannot contain H^+ ions. Urea, $CO(NH_2)_2$, which is neutral in aqueous solution, behaves as an acid in liquid ammonia and as a base in anhydrous acetic acid, although obviously it does not form OH^- ions. Nitric acid, which is a very strong acid in aqueous solution, behaves as a base

when dissolved in liquid HF or in anhydrous H_2SO_4. Many such facts, which do not fit into the framework of the electrolytic dissociation theory, could be cited. They provide evidence of the unsatisfactory nature of the concepts on the nature of acids and bases which have been introduced into science by this theory, and require the replacement of the old views by new and more general ideas which are consistent with experiment.

New theories have therefore been put forward, of which the most widely accepted is the *protolytic theory of acids and bases*, proposed in 1923 by Brönsted and Lowry.

By the protolytic (or proton transfer) theory, *acids are substances (or ions) capable of giving up protons (i. e., proton donors), while bases are substances (or ions) capable of gaining or adding protons (i. e., proton acceptors)*. Since the loss of a proton by an acid is a reversible process, the residue after this loss is capable of gaining a proton, i. e., it is a base. Thus, *every acid has a conjugate base into which it is converted when it loses a proton*:

$$\text{Acid} \rightleftarrows H^+ + \text{Base}$$

Some examples of conjugate pairs of acids and bases are given below:

Acid		*Proton*		*Base*
H_3O^+	$\rightleftarrows$	H^+	+	H_2O
H_2O	$\rightleftarrows$	H^+	+	OH^-
NH_4^+	$\rightleftarrows$	H^+	+	NH_3
CH_3COOH	$\rightleftarrows$	H^+	+	CH_3COO^-
HCl	$\rightleftarrows$	H^+	+	Cl^-
HCO_3^-	$\rightleftarrows$	H^+	+	CO_3^{--}
$H_2PO_4^-$	$\rightleftarrows$	H^+	+	HPO_4^{--}
$Al(OH_2)_6^{+++}$	$\rightleftarrows$	H^+	+	$Al(OH_2)_5OH^{++}$

The following conclusions may be drawn from the foregoing.

(a) The protolytic theory greatly extends the concepts of "acid" and "base". In addition to substances which were formerly regarded as acids (CH_3COOH, HCl, etc.), the term "acid" includes all ions capable of yielding protons, such as HCO_3^-, HSO_4^-, $H_2PO_4^-$, etc. "Anionic" acids of this type are formed from all polybasic acids by partial loss of hydrogen ions. An example of a "cationic" acid is the ammonium ion, NH_4^+, which can lose a proton to form the base NH_3. The cationic acids also include the hydronium ion H_3O^+,

formed by addition of a proton to an H_2O molecule, which gives up that proton very readily to bases such as OH^- ions or anions of weak acids. Others of this class are hydrated cations of certain metals, such as $Al(OH_2)_6^{+++}$, $Fe(OH_2)_6^{+++}$, $Cu(OH_2)_4^{++}$, etc., which lose protons and become the corresponding bases, such as $Al(OH_2)_5OH^{++}$, $Fe(OH_2)_5OH^{++}$, $Cu(OH_2)_3OH^+$, etc. In contrast to cationic and anionic acids, the molecules of the usual acids are uncharged and they are known as "neutral" acids.

(b) Foremost among the bases are OH^- ions, which readily accept protons. All anions capable of accepting protons, such as CO_3^{--}, CN^-, CH_3COO^-, etc., are also bases. The neutralization of acids by carbonates is easily understood from this viewpoint, because carbonates contain the base CO_3^{--} which, like OH^- ions, readily gains protons. An example of a "neutral" base is ammonia, which can gain protons from water, or acid molecules, e.g.:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

$$NH_3 + CH_3COOH \rightleftarrows NH_4^+ + CH_3COO^-, \text{ etc.}$$

(c) The examples given here also show that some substances are capable both of giving up and of adding protons, i. e., they are acids and bases simultaneously. In the terminology of this theory they are known as *amphiprotic substances.* They include water, which can lose a proton to form a base (the OH^- ion), or gain one to form an acid (the hydronium ion H_3O^+). The dual nature of water is also manifested in its dissociation in accordance with the protolytic theory, represented by the equation

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

In this reaction one H_2O molecule loses a proton, thus behaving as an acid, while another gains it, acting as a base. Most other solvents have similar amphiprotic properties. For example, liquid ammonia partially dissociates:

$$NH_3 + NH_3 \rightleftarrows NH_4^+ + NH_2^-$$

Here the NH_4^+ ion has acidic properties while the NH_2^- ion is the carrier of basic properties (analogously to H_3O^+ and OH^- ions in aqueous solutions).

It has been established experimentally that free protons cannot exist in solution. Therefore reactions of proton loss or addition, corresponding to the schematic equation

$$\text{Acid} \rightleftarrows H^+ + \text{Base}$$

do not occur in isolation, but are accompanied by transfer of protons from the acid to a base capable of accepting them. In other words, two processes must occur simultaneously:

$$\text{Acid}_1 = \text{H}^+ + \text{Base}_1$$
$$\text{Base}_2 + \text{H}^+ = \text{Acid}_2$$

Adding these two equations, we obtain the following overall equation for the reaction:

$$\text{Acid}_1 + \text{Base}_2 = \text{Acid}_2 + \text{Base}_1$$

Thus by the protolytic theory, *the interaction of an acid and a base always yields a new acid and a new base.* This is illustrated by the following examples:

$$\begin{array}{cccc} \textit{Acid}_1 & \textit{Base}_2 & \textit{Acid}_2 & \textit{Base}_1 \\ \text{CH}_3\text{COOH} + \text{OH}^- = \text{H}_2\text{O} + \text{CH}_3\text{COO}^- \\ \text{CH}_3\text{COOH} + \text{NH}_3 = \text{NH}_4^+ + \text{CH}_3\text{COO}^- \\ \text{H}_3\text{O}^+ + \text{NH}_3 = \text{NH}_4^+ + \text{H}_2\text{O} \\ \text{HCO}_3^- + \text{OH}^- = \text{H}_2\text{O} + \text{CO}_3^{--} \end{array}$$

It has been shown experimentally (see Sec. 11) that electrolytic dissociation of homopolar acid and base molecules can occur only as the result of their interaction with the solvent, solvated ions being formed. By the present theory, electrolytic dissociation of acids and bases is accordingly interpreted as a typical protolytic (proton transfer) reaction involving the solvent. For example, the dissociation of acetic acid may be represented by the equation*

$$\begin{array}{cccc} \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftarrows \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^- \\ \text{Acid}_1 \quad \text{Base}_2 \quad \text{Acid}_2 \quad \text{Base}_1 \end{array}$$

Here the solvent (H_2O) acts as a base which gains the protons lost by the acetic acid molecules. Bases, on the other hand, gain protons from the solvent molecules and the solvent then acts as an acid. The dissociation of ammonia and of aniline ($C_6H_5NH_2$) in aqueous solution may be represented by the equations:

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftarrows \text{NH}_4^+ + \text{OH}^-$$
$$\begin{array}{cccc} \text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftarrows \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^- \\ \text{Base}_1 \quad \text{Acid}_2 \quad \text{Acid}_1 \quad \text{Base}_2 \end{array}$$

The strength of an acid or base depends primarily on its tendency to lose or gain protons. In addition, the properties of the solvent have

* Of course, this is also a simplified equation, because it disregards hydration of the CH_3COO^- ion, and also the possible further hydration of the hydronium ion H_3O^+.

considerable significance. It is obvious that *under given conditions the more basic the solvent, i. e., the greater its proton affinity, the more dissociated an acid must be. Conversely, the degree of dissociation of a base increases with decrease of the proton affinity of the solvent, i. e., with increasing ease of proton loss by the solvent**.

Many examples could be given to confirm the validity of these conclusions drawn from the protolytic theory of acids and bases. For example, water is a fairly strong basic solvent, having relatively high proton affinity. Accordingly, when strong acids such as $HClO_4$, H_2SO_4, HCl, HNO_3, etc., are dissolved in water, the protolytic equilibrium between the acid (HA) and the solvent (H_2O)

$$\underset{\text{Acid}_1}{HA} + \underset{\text{Base}_2}{H_2O} \rightleftarrows \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{A^-}$$

is shifted almost completely to the right, which corresponds to complete dissociation of these acids in solution. The differences in their tendency to lose protons in aqueous solutions are completely masked by the greater tendency of this solvent to gain protons.

However, if a less basic solvent, such as ethyl alcohol, C_2H_5OH, is taken instead of water the differences between the strengths of the acids become noticeable. In this solvent nitric acid becomes a moderately strong acid. In solvents of even lower proton affinity, such as acetone CH_3COCH_3 or nitrobenzene $C_6H_5NO_2$, all acids which are strong in aqueous solutions, with the exception of $HClO_4$ and H_2SO_4, become moderately strong.

Finally, in anhydrous H_2SO_4, which is a solvent of even lower proton affinity and which therefore has a high tendency to proton loss, only perchloric acid $HClO_4$, which has even lower proton affinity, continues to act as a strong acid. Nitric acid in this solvent behaves as a base, as it gains protons from H_2SO_4 to form nitronium ions $[NO_3H_2]^+$, which are cationic acids similar in composition to ammonium and hydronium ions**. Organic acids, esters, alcohols, and similar compounds are also bases in this solvent.

The reverse relationships are found for solvents with basic properties. For example, in liquid ammonia, which is more basic than water, many acids which are very weak in aqueous solution become quite strong.

As the result of measurements in strongly acidic solvents, acids which are equally strong in aqueous solutions were found to form

---

* It will be remembered that most solvents have amphiprotic properties, and therefore both acids and bases dissociate in them.

** Nitronium perchlorate, $[NO_3H_2]ClO_4$, has been isolated in the solid state.

the following series in the order of decreasing tendency to lose protons:

$$HClO_4 > H_2SO_4 > HCl > HBr > HI > HNO_3$$

From the relationship between acids and bases, expressed in the fundamental equation of the protolytic theory

$$\text{Acid} \rightleftarrows H^+ + \text{Base}$$

it is clear that the strengths of a conjugate acid and base are in an inverse ratio, i.e., *the stronger the acid the weaker its conjugate base, and vice versa.* For example, HCl is a very strong acid, since its molecules have a very pronounced tendency to lose protons, and therefore it is dissociated almost completely in aqueous solution:

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

But it follows from this that the Cl^- ions formed as the result of the dissociation have very low proton affinity, i. e., they are a very weak base. Acetic acid is a weak acid and has a low tendency to lose protons; accordingly, its degree of dissociation in aqueous solution is low. On the other hand, its conjugate base (CH_3COO^-) has a very strong tendency to gain protons and is therefore a strong base.

The protolytic theory, which predicts the behaviour of various substances in non-aqueous as well as aqueous solutions, is a much more general theory of acids and bases than the usual concepts based on the Arrhenius theory of electrolytic dissociation. Moreover, with the aid of this theory it is possible to examine from a unified viewpoint processes which, according to earlier views, are of entirely different types. These include neutralization reactions, interaction between strong acids and salts of weak acids or between strong bases and salts of weak bases, the hydrolysis of salts, and the electrolytic dissociation of acids and bases. The theory establishes an analogy between protolytic reactions and oxidation-reduction reactions, which essentially involve transfer of electrons from atoms (or ions) of the reducing agent to atoms (or ions) of the oxidizing agent. All this demonstrates the valuable advantages of the protolytic theory over earlier views. However, it has not yet gained full acceptance. Its subsequent development would entail the revision of all existing chemical views.

QUESTIONS AND PROBLEMS *

1. Derive the equation for the solubility product of $CaCO_3$ and calculate its numerical value, given that the solubility of $CaCO_3$ is 0.0069 g/litre.

Answer. 4.8×10^{-9}.

* In all the problems the solubilities and solubility products are given for 20°.

2. The solubility of $Fe(OH)_3$ is 2×10^{-8} g/litre. Calculate its solubility product.

Answer. 3.8×10^{-38}.

3. Calculate the solubility product of $CaSO_4$, given that its solubility is 2 g/litre. Take activity coefficients into account.

Answer. 6.5×10^{-5}.

4. Calculate the solubilities of $PbSO_4$ and PbI_2 in moles and grams per litre from their solubility products. Explain why the salt with the smaller solubility product has the higher solubility.

Answer. (a) The solubility of $PbSO_4$: 1.5×10^{-4} *M*; 4.5×10^{-2} g/litre. (b) The solubility of PbI_2: 1.3×10^{-3} *M*; 6.0×10^{-1} g/litre.

5. The solubility product of $Pb_3(PO_4)_2$ is 1.5×10^{-32}. Calculate its solubility in grams per litre and find the concentrations of Pb^{++} and PO_4^{---} ions in a saturated solution.

Answer. 1.37×10^{-4} g/litre; $[Pb^{++}] = 5.1 \times 10^{-7}$ g-ion/litre; $[PO_4^{---}] = 3.4 \times 10^{-7}$ g-ion/litre.

6. The solubility product of $AgBrO_3$ is 5.77×10^{-5}. Find its solubility in moles and in grams per litre (with activity coefficients taken into account).

Answer. 8.1×10^{-3} *M*; 1.91 g/litre.

7. Explain how an unsaturated solution of $AgBrO_3$ can be made saturated and supersaturated at the same temperature without adding more of the same salt.

8. How is the solubility of a sparingly soluble electrolyte affected by the introduction of a common ion into the solution?

9. Calculate the ratio of the solubilities of AgCl in pure water and in 0.01 *M* NaCl solution.

Answer. About 800:1.

10. Solve Problem 9 taking activity coefficients of the ions into account.

Answer. About 690:1.

11. What is the salt effect? How is it explained by the theory of strong electrolytes?

12. How is the solubility of CaC_2O_4 influenced by the presence of 0.1 *M* KCl in solution?

Answer. It is increased in the ratio of 2.17:1.

13. Calculate the ratio of the solubilities of CaC_2O_4 in pure water and in 0.01 *M* $(NH_4)_2C_2O_4$ solution (a) using the simplified formula for *SP*; (b) using the exact formula.

Answer. (a) About 200:1; (b) about 108:1.

14. Use the solubility product rule to state the conditions for (a) precipitate formation; (b) dissolution of precipitates.

15. Find by calculation whether $PbCl_2$ is precipitated when 0.05 *N* $Pb(NO_3)_2$ solution is mixed with an equal volume of (a) 0.05 *N* HCl; (b) 0.5 *N* HCl.

Answer. (a) No; (b) yes.

16. Find by calculation whether $SrSO_4$ is precipitated when equal volumes of 0.001 *N* $SrCl_2$ and K_2SO_4 solutions are mixed.

Answer. No.

17. The solubility of $CaSO_4$ is 2 g/litre. A saturated calcium sulphate solution is mixed with an equal volume of a solution containing 0.0248 g $(NH_4)_2C_2O_4$ per litre. Calculate the ionic product $[Ca^{++}] \cdot [C_2O_4^{--}]$ and find whether CaC_2O_4 is precipitated.

Answer. 7.5×10^{-7}; a precipitate is formed.

18. The S^{--} ion concentration in aqueous hydrogen sulphide solution is 1.2×10^{-15} g-ion/litre.* Calculate from this value and from the solubility

* The method for calculating the concentration of these ions is discussed in Sec. 39.

products of lead chloride and sulphide whether PbS is precipitated when H_2S gas is passed through saturated $PbCl_2$ solution.

Answer. PbS is precipitated.

19. Calculate the weight (in grams) of Pb^{++} remaining in 100 ml of solution if a $Pb(NO_3)_2$ solution is mixed with (a) an equivalent amount of H_2SO_4; (b) excess H_2SO_4 calculated to give a concentration of 0.01 *M* at the end of precipitation.

Answer. (a) 3.1×10^{-3} g; (b) 4.6×10^{-5} g.

20. Why is the precipitant used in excess in precipitation reactions? Why is too large an excess not recommended?

21. Give examples to illustrate the influence of the degree of dissociation of the precipitant on the completeness of precipitation. How can precipitation be prevented?

22. Describe and explain the effect of hydrolysis of $(NH_4)_2CO_3$ on the completeness of precipitation of Group II cations. How can the influence of hydrolysis be diminished?

23. $AgNO_3$ solution is added to a solution containing Cl^- and I^- ions. If the concentrations of these ions are both 0.01 g-ion/litre, which salt—AgCl or AgI—is formed first? State the concentration ratio at which both salts are precipitated together.

Answer. AgI; $[Cl^-] : [I^-] \approx 1{,}000{,}000$.

24. $(NH_4)_2C_2O_4$ solution is added to a solution containing 1 g-ion of Ba^{++} and 0.01 g-ion of Ca^{++} per litre. Which of the cations is the first to be precipitated, and what percentage of it is precipitated when precipitation of the other cation begins?

Answer. Ba^{++}; 38%.

25. A mixture of equal volumes of $(NH_4)_2C_2O_4$ and Na_2SO_4 solutions of equal normality is added to a solution containing Ba^{++} and Ca^{++} ions in equal concentrations. What compounds are precipitated?

26. State the condition for conversion of a $BaCrO_4$ precipitate into $BaCO_3$ by the action of Na_2CO_3 solution. What is the ratio of the CO_3^{--} and CrO_4^{--} ion concentrations at equilibrium?

Answer. $[CO_3^{--}] : [CrO_4^{--}] = 33.3$.

27. What should be done in order to dissolve a precipitate? How can the following substances, sparingly soluble in water, be dissolved: $Al(OH)_3$, H_2WO_4, FeS, $BaCrO_4$?

28. Give examples of processes which can cause binding of ions, leading to dissolution of precipitates.

REACTIONS AND ANALYTICAL PROCEDURE FOR GROUP II CATIONS

32. General characteristics of Group II cations

Cations of analytical Group II include Ca^{++}, Sr^{++} and Ba^{++}. In contrast to most of the Group I cations, these ions form a number of sparingly soluble salts with various anions. For example, the sulphates, phosphates, oxalates and carbonates of Group II metals are sparingly soluble. In the form of which salts should Group II be separated from Group I? The answer to this question is determined by a number of considerations. First, the salts must be sufficiently insoluble, i.e., they should have the lowest possible solubility products. For example, Group II could not be precipitated

completely in water solutions in the form of sulphates, as one of them ($CaSO_4$) has a fairly large* solubility product (5.6×10^{-5}). Another disadvantage is that sulphates, being salts of a strong acid, are practically insoluble in acids and it would therefore be relatively difficult to dissolve them after separation from Group I.

It is also difficult to separate Group II in the form of phosphates or oxalates, as the PO_4^{---} and $C_2O_4^{--}$ ions introduced into the solution would complicate the subsequent analysis.

The most suitable procedure is to separate Group II cations from Group I in the form of carbonates—$CaCO_3$, $SrCO_3$ and $BaCO_3$. The solubility products of these salts are small (of the order of 10^{-9}), and therefore practically complete precipitation of all the Group II cations is possible. Moreover, it is very simple to dissolve the precipitate for further analysis of Group II because, in contrast to sulphates, Group II carbonates are readily soluble in acids, being salts of a weak acid. Finally, the excess of the precipitant CO_3^{--} ions is easily removed when the solution is acidified, because the carbonic acid formed decomposes into CO_2 and H_2O.

From this it follows that *the most important analytical property of Group II cations, used for separating them from Group I, is the practical insolubility of the carbonates* $CaCO_3$, $SrCO_3$, *and* $BaCO_3$ *in water.*

*On the other hand, the sulphides of Group II cations***, *like those of Group I, are soluble in water; this distinguishes Group II from Groups III, IV, and V.*

The Group II carbonates are precipitated when the ionic product $[Me^{++}] \cdot [CO_3^{--}]$ in solution exceeds the solubility product of $MeCO_3$ (Me^{++} represents any Group II cation). However, *only ammonium carbonate*, $(NH_4)_2CO_3$, *can be used as the group reagent for Group II*, because the use of Na_2CO_3 or K_2CO_3 would introduce Na^+ or K^+ ions, so that these ions could not be tested for in the solution remaining after separation of the precipitate. The introduction of the ammonium ion does not lead to error, because ammonium is detected in a separate portion of the solution before the addition of the Group II reagent.

---

* It should be noted, however, that the solubility of $CaSO_4$ is greatly reduced by addition of ethyl alcohol; this is sometimes utilized in analysis (see p. 176).

** The least soluble is CaS, a saturated solution of which contains about 2 g of the salt per litre at room temperature. However, like all the other Group II sulphides, it is almost completely hydrolyzed in aqueous solution to give a soluble hydrosulphide and the hydroxide:

$$2CaS + 2H_2O \rightleftarrows Ca(HS)_2 + Ca(OH)_2$$

Therefore Ca^{++}, like all the other Group II and I sulphides, is not precipitated by S^{--} ions in aqueous solution.

All the metals of Group II also belong to the second group of the periodic system; they are in the first half of the long period, i.e., in the even rows. They are known as the alkaline earth metals; they decompose water rapidly at room temperature:

$$Ca^{++} + 2H_2O = Ca(OH)_2 + H_2\uparrow$$

The chemical activity increases in the series from Ca to Ba. Many other properties, such as the solubility of their salts, the basic properties of the hydroxides, etc., vary in the same direction.

Since their basic properties are very pronounced, the salts formed by Group II metals and strong acids are not hydrolyzed to any appreciable extent and are almost neutral in solution (pH $\approx$ 6).

Like the Group I cations, the Ca^{++}, Sr^{++} and Ba^{++} ions have complete outer shells of 8 electrons. These ions are colourless in aqueous solutions.

33. Action of the Group Reagent

As in every group separation, Group II cations should be precipitated by the group reagent $(NH_4)_2CO_3$ under conditions ensuring complete separation from Group I cations. One of the most important conditions for complete precipitation of sparingly soluble salts of weak acids, such as the carbonates of Group II cations, is a suitable solution pH.

It was shown in Sec. 26 that in this instance the pH is predetermined to a considerable extent by the presence of excess $(NH_4)_2CO_3$, which is hydrolyzed almost completely in solution:

$$(NH_4)_2CO_3 + H_2O \rightleftarrows NH_4HCO_3 + NH_4OH$$

or

$$NH_4^+ + CO_3^{--} + H_2O \rightleftarrows HCO_3^- + NH_4OH$$

Because of this, ammonium carbonate solution is really a mixture of approximately equivalent amounts of NH_4OH and the ammonium salt NH_4HCO_3, i.e., it is an ammonium buffer mixture of pH $\approx$ 9.2. At this pH all three Group II carbonates are precipitated almost completely (see p. 131), while the K^+, Na^+ and NH_4^+ cations, which form soluble carbonates, remain in solution.

Although basic magnesium carbonate $(MgOH)_2CO_3$ and magnesium hydroxide $Mg(OH)_2$ are sparingly soluble, they are not precipitated either at pH $\approx$ 9.2. It was shown earlier (p. 126) that precipitation of $Mg(OH)_2$ begins at pH $>$ 9.3 and is complete at pH = 11.3. The conditions for precipitation of $(MgOH)_2CO_3$ are similar.

Thus, *Groups II and I cations are separated completely when the precipitation is performed at* pH $\approx$ 9.2. At pH $<$ 9.2 the precipitation of Group II cations is incomplete, while at pH $>$ 9.3 Mg^{++} is partially precipitated.

It might appear that the pH required for precipitation of Mg^{++} would arise owing to the presence of excess $(NH_4)_2CO_3$. In reality this is true only if the buffer capacity of the solution is sufficient, i.e., if the solution is capable of consistently maintaining a constant pH (p. 77).

The following considerations show that the buffer capacity of the solution must be taken into account in this case. Ammonium carbonate solution is a mixture of equivalent amounts of NH_4OH and NH_4HCO_3 (i.e., HCO_3^- ions). Therefore the reaction which takes place when Group II cations are precipitated by ammonium carbonate is essentially represented by the equation

$$MeCl_2 + NH_4HCO_3 + NH_4OH = \downarrow MeCO_3 + 2NH_4Cl + H_2O$$

or, in ionic form

$$Me^{++} + HCO_3^- + NH_4OH = \downarrow MeCO_3 + NH_4^+ + H_2O$$

The equation shows that NH_4OH is used up in the reaction while NH_4^+ ions accumulate in the solution. Similar consumption of ammonia and accumulation of NH_4^+ ions must evidently occur if ammonium carbonate reacts with any acids which may be present in the solution:

$$2H^+ + HCO_3^- + NH_4OH = \uparrow CO_2 + 2H_2O + NH_4^+$$

The pH of an ammonium buffer mixture is given by the formula (p. 75):

$$pH = 14 - pK_{NH_4OH} + \log \frac{[NH_4OH]}{[NH_4^+]} = 9.25 + \log \frac{[NH_4OH]}{[NH_4^+]} \qquad (1)$$

As NH_4OH is used up while NH_4^+ ions accumulate in solution, the ratio of their concentrations decreases and becomes less than unity. Accordingly, the solution pH falls to below 9.25.

If this fall of pH is at all considerable, i.e., if the buffer capacity of the solution is inadequate, the precipitation of Group II cations is incomplete. However, it was shown in Sec. 16 that the buffer capacity of a buffer mixture increases with increasing concentration of its components. For example, the buffer capacity of a 1 *N* ammonium buffer mixture is much greater than that of 0.1 *N**, while that of 0.01 *N* is stiil lower. While even relatively large changes in the concentrations of NH_4OH and NH_4^+ ions have very little effect

* See Table 8, p. 78.

on the pH of 1 *N* buffer mixture, they can produce very sharp pH changes in the case of 0.1 or 0.01 *N* buffer mixture.

Therefore it is not enough to introduce a buffer mixture (for example, ammonium carbonate solution) with the required pH; it is necessary to ensure that its buffer capacity is sufficient. In practice, before precipitation of Group II cations by ammonium carbonate, ammonia is added to the solution until an odour appears (or to an alkaline reaction), followed by a little NH_4Cl. Ammonia neutralizes any free acids, but the solution becomes so alkaline that Mg^{++} may be precipitated. Addition of NH_4Cl lowers the pH to the required value of ~9 (this should be confirmed with indicator paper). At the same time the buffer capacity of the solution is raised by the addition of ammonia and ammonium chloride to such an extent that the consumption of NH_4OH and accumulation of NH_4^+ ions cannot produce any appreciable changes of solution pH.

Another condition influencing the completeness of precipitation of Group II cations is the temperature of the solution. The reason is that solid ammonium carbonate partially decomposes on keeping, liberating water and forming a substance known as ammonium carbamate (a salt of carbamic acid, NH_2COOH). The equation for this reaction is

$$(NH_4)_2CO_3 \rightleftarrows NH_2COONH_4 + H_2O$$

Therefore commercial ammonium carbonate usually contains carbamate, which lowers considerably the CO_3^{--} ion concentration in its solutions. However, this effect is easily prevented if the precipitation of Group II is performed in solution heated to about 80°, as at higher temperatures the equilibrium of the above reaction is shifted to the left, towards conversion of ammonium carbamate into carbonate. Heating is also useful because it accelerates the conversion of the originally amorphous carbonate precipitate into a crystalline form, which is easier to filter off and which has less tendency to adsorb extraneous ions.

It follows that *Group II cations should be precipitated by the group reagent in the presence of ammonia and ammonium chloride (at* pH = *9.2) in a solution heated to 80°*. $CaCO_3$, $SrCO_3$ and $BaCO_3$ are precipitated while the Group I cations and the added ammonium salts remain in solution.

Study the action of the group reagent experimentally.

1. Add ammonium carbonate to solutions of $CaCl_2$, $SrCl_2$ and $BaCl_2$ and examine the precipitates. They are all white.

The reaction (with calcium salts) is

$$CaCl_2 + (NH_4)_2CO_3 = \downarrow CaCO_3 + 2NH_4Cl$$

or, in ionic form

$$Ca^{++} + CO_3^{--} = \downarrow CaCO_3$$

2. Add K_2CO_3 or Na_2CO_3 solution to the same solutions. Write down the equations for the reactions.

3. Treat the precipitates obtained in the first two experiments with acids, such as HCl, HNO_3, or CH_3COOH. The equation (for $CaCO_3$) is

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2 \uparrow$$

or

$$CaCO_3 + 2H^+ = Ca^{++} + H_2O + CO_2 \uparrow$$

The dissolution of $CaCO_3$ and other carbonates in acids is due to the formation of carbonic acid (H_2CO_3), which dissociates very little, and, moreover, decomposes as soon as it forms to liberate CO_2 gas.

4. Confirm that $CaCO_3$ is appreciably soluble in excess NH_4Cl. To 1-2 drops of $CaCl_2$ solution add an equal volume of $(NH_4)_2CO_3$ solution followed by a large excess of NH_4Cl. The $CaCO_3$ precipitate dissolves*.

34. Techniques of Separation Reactions

In precipitation of Group II cations we meet the group separation procedure for the first time. As already stated, this operation (like the separation of individual ions) is of very great importance in analysis. Therefore we must consider the techniques used more fully.

First, when carrying out any separation we must make sure to take enough of the precipitating reagent, $(NH_4)_2CO_3$ in this case, as otherwise the precipitation would be incomplete and the object of the whole operation would not be achieved.

It is very easy to find how much reagent to take by a simple experiment or *test for complete precipitation.*

To carry out this test, first add to the solution an arbitrary amount of the reagent, filter off a few millilitres of the liquid into a test tube, and add a small amount of the same reagent, i.e., $(NH_4)_2CO_3$, to the filtrate. If the separation is complete no precipitate forms and the liquid remains clear. On the other hand, a precipitate (or turbidity) indicates that not enough reagent was taken. In that case add a further portion to the whole solution and repeat the test for complete precipitation. Continue in this manner until the last

---

* Group II carbonates are soluble in NH_4Cl because ammonium chloride has an acid reaction as the result of hydrolysis. It was shown earlier that acids dissolve these carbonates.

test shows absence of the precipitated ions in solution. In some cases a special test for complete precipitation may be superfluous, because sometimes the colour of the solution, its reaction or other signs indicating the presence of excess precipitant may show that the precipitation is complete. For example, in the separation of Ba^{++} as $BaCrO_4$ (Sec. 38-7), the orange-yellow colour of the solution due to the reagent (K_2CrO_4) is a sign of complete precipitation.

Similarly, when hydroxides are precipitated by the action of alkalies on their salts, for example

$$FeCl_3 + 3KOH = \downarrow Fe(OH)_3 + 3KCl$$

when the solution becomes alkaline an excess of the KOH used for precipitation is present and it may be concluded that the precipitation is complete.

In general, in any separation it is imperative to confirm by one method or another that the separation is complete. Only then will the results of the analysis be correct.

The precipitation conditions are also very important in separation reactions. The precipitate must be filtered off, but in some reactions the precipitates formed are so fine that their particles pass freely through the filter pores and the filtrates are turbid. Sometimes this turbidity cannot be eliminated even by repeated filtration of the liquid through the same filter. Even if a transparent filtrate is obtained, the filtration of microcrystalline precipitates is very slow, as the particles block the filter pores.

It follows that in separation reactions it is necessary to obtain sufficiently coarse-grained precipitates. As was pointed out in Sec. 3, such precipitates are obtained from *weakly supersaturated solutions*, as under these conditions the number of crystal nuclei formed is relatively small and they can grow into fairly large crystals. The following conditions must be satisfied in order that the solution should be only slightly supersaturated with the precipitated compound.

(a) The precipitation must be performed from dilute solution by a dilute solution of the precipitant.

(b) The precipitant must be added slowly—drop by drop or in a thin stream, with continuous stirring by means of a glass rod.

(c) The solubility of the compound formed should be increased by conducting the precipitation in heated solution or by addition of an appropriate reagent (for example, HCl in the precipitation of $BaSO_4$). This higher solubility must later be lowered by addition of excess reagent or in some other way; otherwise the precipitation will be incomplete.

It must be remembered that quite often some time elapses before the precipitation is complete. Therefore crystalline precipitates are

left to stand before filtration. This is also advantageous because the precipitate grains increase in size on standing.

Research has shown that smaller crystals are always somewhat more soluble than larger ones. Therefore small crystals gradually dissolve while the larger ones grow correspondingly. These processes are associated with diffusion of the crystallizing substance in solution. This diffusion is more rapid at higher temperatures, when the molecules move more rapidly. Therefore large crystals grow at the expense of smaller ones much more rapidly on heating than in the cold. Consequently it is preferable to allow the precipitates to stand in a warm place; for example, the beaker with the precipitate can be stood on a water bath, etc.

It should be pointed out that in some cases not all the above conditions are equally important, and some may be disregarded in some instances. When Group II cations are precipitated as the carbonates, $(NH_4)_2CO_3$ may be all added at once rather than drop by drop. This is permissible because after the precipitation the liquid with the precipitate must be heated for some time to decompose the ammonium carbamate present. When this is done, the precipitate very rapidly becomes coarse-grained, no matter how fine it was when first formed. On the other hand, substances which pass very readily through filters, such as $BaSO_4$ or $BaCrO_4$, must always be precipitated from solutions heated to boiling, the precipitant being added drop by drop.

In the case of amorphous precipitates, it must be remembered that many of them tend to form colloidal solutions which pass through the filter. To prevent this effect it is necessary to ensure (as is explained fully in Sec. 41) that a suitable coagulating electrolyte is present in solution, and to precipitate from hot solution.

When the precipitation is complete and the precipitate has been left to settle, the next step is *filtration*. In order that this operation should take up as little of the analyst's time as possible, it should be carried out as follows.

First, choose a filter of suitable size and fit it correctly in the funnel.

The choice of filter size *must be guided by the amount of precipitate* and not the volume of liquid to be filtered. Too large a filter is unsuitable, because it must subsequently be washed to remove adsorbed substances. Obviously, more time is needed for such washing in the case of large filters. On the other hand, the filter must not be too small either, as it would be impossible to wash the precipitate thoroughly (see below). In any event, the precipitate should not occupy more than half the volume of the filter.

The paper used for filtration (*filter paper*) is usually cut in square pieces. To prepare a filter, fold the piece of paper in half and then

in half again at right angles to the first fold. This gives a square of one-quarter the original size; cut this along an arc to form a sector (Fig. 18). In this sector separate one layer of paper from the other three to form a cone and insert this in the funnel. This paper cone

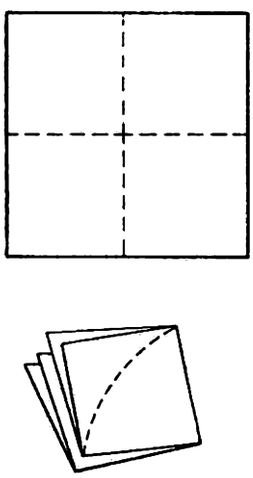


Fig. 18. Preparing the filter

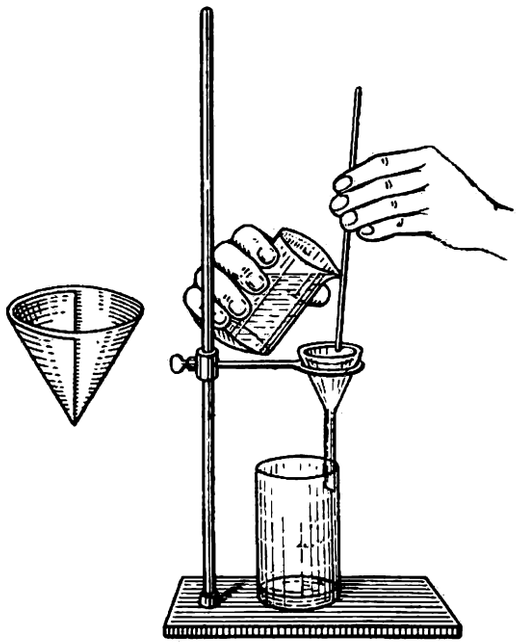


Fig. 19. Filtration

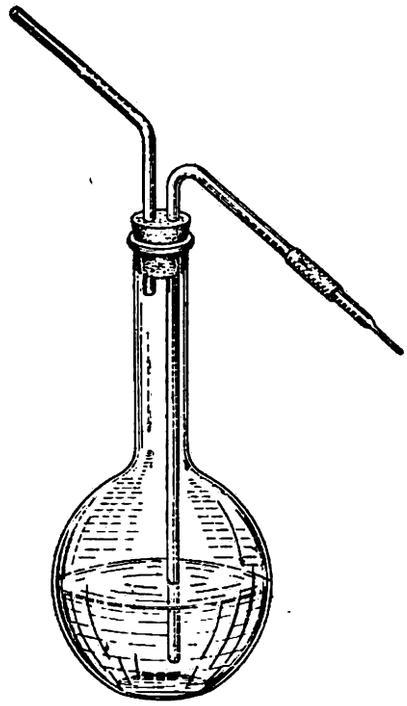


Fig. 20. Wash bottle

should fit closely to the funnel over its whole surface. If it does not, displace the paper layers relative to each other to increase or decrease the base of the cone. When the cone fits exactly, insert it into the funnel, moisten with water, and press it cautiously with a clean finger against the glass. Try to ensure that no air bubbles remain between the paper and the funnel. If this is done, the stem of the funnel usually fills completely with filtrate, which drags down the liquid in the filter by its weight, so that filtration is accelerated considerably. On the other hand, if the filter does not fit snugly the air bubbles entering the funnel stem slow down the movement of the filtrate through it.

To avoid splashing, pour the liquid into the filter down a glass rod held against the lip of the beaker (Fig. 19). For the same reason the bevelled tip of the funnel stem should be in close contact with the wall of the beaker in which the filtrate is collected. For more rapid filtration first pour the clear supernatant liquid into the filter and transfer the precipitate into it only at the end.

After the filtration the precipitate collected on the filter must be washed, because it contains the solution from which it was precipitated; this solution contains cations which are to be separated

from the precipitate on the filter, so that unless the precipitate is washed the separation is not achieved; the same solution also contains excess precipitant. Another purpose of washing is to remove adsorbed impurities from the precipitate.

Washing is usually carried out with distilled water, generally hot (unless otherwise stated), as hot liquids filter more rapidly than cold because their viscosity decreases with rise of temperature. For example, at 100° water filters twice as fast as at 20° and four times as fast as at 0°. Sometimes when pure water is used the precipitate passes through the filter owing to the formation of a colloidal solution (see Sec. 41 for details). In such cases the precipitate must be washed not with pure water but with an electrolyte solution, usually an ammonium salt, as the introduction of the ammonium ion does not interfere with subsequent analysis.

The wash liquid is usually contained in a wash bottle, illustrated in Fig. 20.

Air is blown by mouth through the short tube of the wash bottle, and a fine jet of liquid is forced out through the pointed tip of the long tube; this is directed on the filter with the precipitate.

Before the filter is refilled with the wash liquid, the previous portion must be allowed to drain off completely. Washing is speeded up considerably in this way, as the amount of impurities remaining on the filter decreases rapidly*.

With crystalline precipitates it is usually sufficient to fill the filter four or five times with the wash liquid. Amorphous precipitates require longer washing, because they adsorb large amounts of dissolved substances from solutions in contact with them.

Of course, thorough washing of precipitates is not always necessary. For example, in the present instance Group I cations do not interfere with the detection of Group II cations and it is quite sufficient to fill the filter once or twice. In other cases, however, the washing must be continued until a negative reaction is obtained

---

* This is illustrated by the following numerical example. Suppose that 10 ml of water is poured on the filter each time; 9 ml filters through and 1 ml remains in the precipitate and filter pores. If the original amount of impurity removable by washing is 0.1 g, then

	Removed	*Remains*
After the first wash	0.09 g	0.01 g
After the second wash	0.009 g	0.001 g
After the third wash	0.0009 g	0.0001 g
After the fourth wash	0.00009 g	0.00001 g

etc. The advantage of this method of washing is obvious.

On the other hand, if the filter is filled after one half of the liquid in it has drained off we have a progression with a common ratio of 1/2 instead of 1/10, and the washing takes much longer.

for ions which interfere with any subsequent reactions. Separate portions of the washings are collected from the filter from time to time in a clean test tube and tested for the ion being removed with the appropriate reagent. Obviously in such cases washing of precipitates cannot be neglected as is often done by beginners who hope to speed up their work in this way. In reality, the work is often slowed down instead because, owing to incomplete removal of extraneous ions from the precipitate, many tests give indistinct and confusing results. The analysis thus proves incorrect and has to be repeated.

So that the filtrate is not diluted, the washings are collected in a separate vessel and discarded at the end of the washing.

The washed precipitate is usually dissolved in a suitable reagent. If it is easily dissolved, the operation is performed without removing the precipitate from the filter. Otherwise the precipitate is first removed from the filter with a glass rod or spatula and finally washed down with a strong stream of water from the wash bottle into the vessel where it is to be dissolved.

35. Reactions of the Ba^{++} Cation

1. Potassium dichromate, $K_2Cr_2O_7$, forms a yellow precipitate of $BaCrO_4$ with Ba^{++}, and not $BaCr_2O_7$ as might be expected. The reason is this. A solution of $K_2Cr_2O_7$ contains, in addition to $Cr_2O_7^{--}$, a small amount of CrO_4^{--} ions formed by the interaction of $Cr_2O_7^{--}$ with water:

$$Cr_2O_7^{--} + H_2O \rightleftarrows 2CrO_4^{--} + 2H^+$$

However, the CrO_4^{--} concentration is high enough to exceed the solubility product of $BaCrO_4$ *before the solubility product of barium dichromate,* $BaCr_2O_7$, *is reached.* Therefore $BaCrO_4$ is the compound precipitated:

$$2CrO_4^{--} + 2Ba^{++} = \downarrow 2BaCrO_4$$

Adding the two equations (and cancelling out $2CrO_4^{--}$), we have the overall equation for the reaction:

$$Cr_2O_7^{--} + 2Ba^{++} + H_2O \rightleftarrows \downarrow 2BaCrO_4 + 2H^+$$

In the molecular form this equation becomes

$$K_2Cr_2O_7 + 2BaCl_2 + H_2O \rightleftarrows \downarrow 2BaCrO_4 + 2KCl + 2HCl$$

The $BaCrO_4$ precipitate is soluble in strong acids but not in acetic acid (test this). Since a strong acid (HCl) is formed as the result of the reaction itself, the reaction does not go to completion. However,

complete precipitation of Ba^{++} can be achieved if CH_3COONa is added as well as $K_2Cr_2O_7$; the strong acid (HCl) is then replaced by the weak acetic acid (Sec. 30), in which $BaCrO_4$ is insoluble:

$$CH_3COONa + HCl = CH_3COOH + NaCl$$

Excess CH_3COONa should be taken, so that a part of it remains unused, i.e., so that an acetate buffer mixture is formed. This maintains the pH, despite the formation of H^+ ions in the reaction, practically constant at about 5, which is necessary for complete precipitation of $BaCrO_4$.

Sr^{++} and Ca^{++} ions are not precipitated by $K_2Cr_2O_7$ and therefore do not interfere with the detection of Ba^{++}. This reaction is used not only for detection of Ba^{++}, but also for its separation from Ca^{++} and Sr^{++}.

A precipitate of $BaCrO_4$ is also formed by the action of potassium chromate on solutions of barium salts. However, K_2CrO_4 gives a yellow precipitate of $SrCrO_4$ with Sr^{++}, which differs from $BaCrO_4$ only by being soluble in acetic acid. Therefore to prevent the formation of $SrCrO_4$ this reaction should be carried out in the presence of CH_3COOH. The H^+ ions of acetic acid combine with CrO_4^{--} ions to give $HCrO_4^-$ anions and thereby lower the chromate ion concentration so much that the ionic product $[Sr^{++}] \cdot [CrO_4^{--}]$ does not reach the solubility product of $SrCrO_4$ and the latter is not precipitated. On the other hand, the solubility product of the less soluble barium chromate is exceeded even in the presence of CH_3COOH, which therefore does not prevent its precipitation.

2. Sulphuric acid and soluble sulphates (SO_4^{--} ions) give a white precipitate of $BaSO_4$ with Ba^{++}:

$$Ba^{++} + SO_4^{--} = \downarrow BaSO_4$$

Being a sparingly soluble salt of a strong acid, barium sulphate is insoluble in acids (test this). To dissolve $BaSO_4$ it is first converted into $BaCO_3$ and the latter is then dissolved in an acid:

$$BaSO_4 + Na_2CO_3 \rightleftarrows BaCO_3 + Na_2SO_4$$

$$BaCO_3 + 2CH_3COOH = (CH_3COO)_2Ba + H_2O + CO_2 \uparrow$$

This is done in practice by heating $BaSO_4$ with a saturated (see Sec. 38-3) solution of sodium carbonate (*wet method*).

However, as $BaSO_4$ is less soluble than the $BaCO_3$ formed, this reaction is reversible (Sec. 29) and can be taken to completion only by repeated treatment of the precipitate with Na_2CO_3 solution. The liquid (containing the SO_4^{--} ions formed in the reaction) is decanted from the precipitate and replaced with a fresh portion of Na_2CO_3 solution; this is repeated several times.

Barium sulphate can also be converted into the carbonate by fusion in a crucible with 5-6 times the amount of a mixture of Na_2CO_3 and K_2CO_3 (*dry method*). A mixture of carbonates is used because it melts at a lower temperature than the individual components. After the mass in the crucible has melted it is allowed to cool; the crucible is then put in a basin with water and heated until the precipitate crumbles to a fine powder and thus enters the basin. The Na_2SO_4 and K_2SO_4 formed in the reaction, together with excess Na_2CO_3 and K_2CO_3, dissolve in water while $BaCO_3$ remains in the residue. The residue is separated from the solution, washed thoroughly*, and dissolved in acid.

3. **Ammonium oxalate,** $(NH_4)_2C_2O_4$, the ammonium salt of oxalic acid $H_2C_2O_4$ (structural formula $\begin{matrix}COOH\\|\\COOH\end{matrix}$) forms a white precipitate of BaC_2O_4 with Ba^{++}:

$$Ba^{++} + C_2O_4^{--} = \downarrow BaC_2O_4$$

The precipitate is soluble in HCl and HNO_3, and when boiled with CH_3COOH.

4. **Disodium hydrogen phosphate,** Na_2HPO_4, forms with Ba^{++} a white precipitate of $BaHPO_4$, soluble in HCl, HNO_3 and CH_3COOH

$$Ba^{++} + HPO_4^{--} = \downarrow BaHPO_4$$

If the reaction is carried out in the presence of caustic alkalies or ammonia, the HPO_4^{--} ions are converted into PO_4^{---} and the neutral salt is precipitated

$$HPO_4^{--} + OH^- = PO_4^{---} + H_2O$$
$$3Ba^{++} + 2PO_4^{---} = \downarrow Ba_3(PO_4)_2$$

Acids have the same effect on this precipitate as on $BaHPO_4$.

5. **Microcrystalloscopic test.** Warm a drop of a slightly acidified solution of a barium salt gently on a glass slide, and immediately add, on the end of a glass rod, a grain of ammonium fluosilicate** $(NH_4)_2[SiF_6]$: crystals of $Ba[SiF_6]$ are formed. They are in the form of small needles or lenses, often in clusters (Fig. 21). As little as 0.1 μg Ba^{++} can be detected by this test. The dilution limit is 1:10,000.

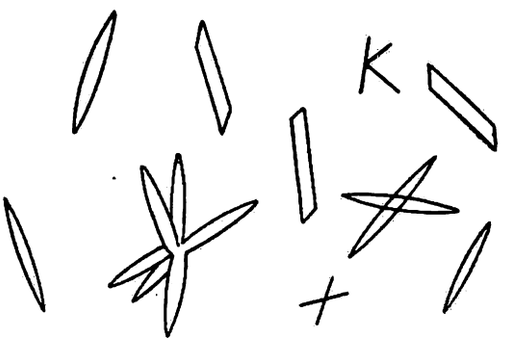


Fig. 21. Crystals of $Ba[SiF_6]$

* Otherwise when the precipitate is dissolved some of the Ba^{++} ions will be precipitated again by the SO_4^{--} ions not removed by washing.

** A salt of fluosilicic acid, $H_2[SiF_6]$.

Sr^{++} and Ca^{++} do not interfere with detection of Ba^{++} if present in not too large amounts. No free HCl or HNO_3 must be present.

6. Flame test. Volatile barium salts, such as $BaCl_2$, $Ba(NO_3)_2$, etc., give a yellow-green colour to a colourless flame.

36. Reactions of the Sr^{++} Cation

1. Sulphuric acid and soluble sulphates form a white precipitate of $SrSO_4$ practically insoluble in acids (why?). It can be dissolved in the same way as $BaSO_4$. As $SrCO_3$ is less soluble than $SrSO_4$, the conversion of sulphate to carbonate is very much easier than in the case of $BaSO_4$ (Sec. 29).

2. Gypsum water, a saturated aqueous solution of $CaSO_4 \cdot 2H_2O$, also gives a precipitate (or turbidity) of $SrSO_4$ with the Sr^{++} ion.

The reason is that although gypsum is only slightly soluble in water its solubility product (6.1×10^{-5}) is considerably larger than that of $SrSO_4$ (2.8×10^{-7}). Therefore the SO_4^{--} ion concentration in a saturated $CaSO_4$ solution is enough to exceed the solubility product of $SrSO_4$. However, since the SO_4^{--} concentration is very low the reaction does not give an abundant precipitate but merely a slight turbidity due to $SrSO_4$ which is usually *delayed* (formation of a supersaturated solution). The turbidity appears more rapidly if the solution is heated.

As the solubility product of $BaSO_4$ (1.1×10^{-10}) is even less than that of $SrSO_4$, barium salts also give a turbidity of $BaSO_4$ with gypsum water, and in this case the turbidity is usually *immediate**. Therefore *the test with* $CaSO_4$ *may be used for detection of* Sr^{++} *only after separation of* Ba^{++}.

3. Disodium hydrogen phosphate, Na_2HPO_4, forms a white precipitate of strontium hydrogen phosphate with Sr^{++}. It is soluble in acids (including acetic):

$$Sr^{++} + HPO_4^{--} = \downarrow SrHPO_4$$

4. Ammonium oxalate, $(NH_4)_2C_2O_4$, gives a white precipitate with Sr^{++}:

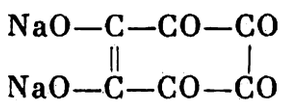
$$Sr^{++} + C_2O_4^{--} = \downarrow SrC_2O_4$$

5. Detection of Sr^{++} and Ba^{++} by the spot test with sodium rhodizonate, $Na_2C_6O_6$.** Put a drop of a neutral solution of a strontium

---

* The rate of formation of $SrSO_4$ and $BaSO_4$ precipitates depends not only on the solubility products but also on the Sr^{++} and Ba^{++} concentrations.

** Its structural formula is



salt on filter paper, and add a drop of aqueous sodium rhodizonate solution. A red-brown spot of precipitated strontium rhodizonate, SrC_6O_6, appears on the paper. When moistened with a drop of dilute HCl the precipitate dissolves and the spot disappears.

The Ba^{++} ion gives a similar red-brown precipitate of BaC_6O_6 with rhodizonate, but this is easily distinguished from strontium rhodizonate, because HCl turns it rose-red owing to conversion into acid barium rhodizonate.

This test is very convenient for fractional detection of Sr^{++} and Ba^{++} in the presence of all other Group II and I cations (no cations of any other groups must be present).

Put a drop of the neutral solution to be tested on a strip of paper and moisten it with a drop of rhodizonate solution. By the side of it put a drop of rhodizonate solution and compare the colours. If they are the same, both Ba^{++} and Sr^{++} are absent. If the spot is red-brown, moisten it with a drop of 0.5 *N* HCl solution (*not stronger*)*. If the spot is decolourized, Ba^{++} is absent and Sr^{++} is present. If the spot turns red (or, more accurately, pink), Ba^{++} is present. In that case test for Sr^{++} as follows. Moisten a strip of paper with K_2CrO_4 solution and put a drop of the unknown solution in the middle of the spot. This precipitates Ba^{++} as $BaCrO_4$, which does not react with rhodizonate. To make sure that precipitation is complete moisten the spot once again with K_2CrO_4, and then put on a drop of rhodizonate. The spot readily turns a brownish-red colour in the presence of Sr^{++}, and orange in its absence (the colour of the control spot formed when a drop of the reagent is put on paper).

Fig. 22. Crystals of $K_2Sr[Cu(NO_2)_6]$

6. Microcrystalloscopic test. Evaporate a drop of strontium salt solution to dryness on a glass slide. Dissolve the dry residue in a drop of 2% $Cu(NO_3)_2$ solution and evaporate to dryness again. When cool, add two drops of 0.05 *N* acetic acid and add a few small crystals of KNO_2 to the clear solution. After a few minutes (or sooner with gentle warming)

* It must be remembered that with small amounts of Ba^{++} the spot may disappear if the amount or the concentration of HCl is greater, and Ba^{++} will be missed. In case of doubt it is useful to carry out an additional test for Ba^{++} with K_2CrO_4 solution.

small blue-green cubes of the triple nitrite $K_2Sr[Cu(NO_2)_6]$ are formed (Fig. 22). The dilution limit is 1:10,000. Crystals of a different shape (green in colour) are formed with Ba^{++} and Ca^{++}.

7. Flame test. Volatile strontium salts confer a characteristic crimson colour to a colourless flame.

37. Reactions of the Ca^{++} Cation

1. Ammonium oxalate, $(NH_4)_2C_2O_4$, gives a white precipitate of calcium oxalate with Ca^{++}. This is soluble in mineral acids but not in acetic acid:

$$Ca^{++} + C_2O_4^{--} = \downarrow CaC_2O_4$$

The presence of Ba^{++} *and* Sr^{++} *ions interferes with this reaction, which is the most important qualitative test for* Ca^{++}; as was shown above, these ions form similar precipitates with $(NH_4)_2C_2O_4$. Calcium oxalate, CaC_2O_4, dissolves in strong acids but not in acetic acid for the following reason.

As was stated in Sec. 28, for a precipitate to dissolve one of the ions which it yields in solution must form a compound of a low degree of dissociation with one of the ions of the reagent dissolving the precipitate. The only compound of this kind possible in this case can be free oxalic acid, $H_2C_2O_4$, formed in accordance with the equation

$$CaC_2O_4 + 2HCl = CaCl_2 + H_2C_2O_4$$

since the other reaction product, $CaCl_2$, is a completely dissociated salt. However, oxalic acid is not a very weak acid. For example, in 0.1 *N* solution it is about 30% dissociated. If, despite this, CaC_2O_4 nevertheless dissolves in strong acids, this is only because we introduce with these acids a large amount of H^+ ions, which greatly depress the dissociation of $H_2C_2O_4$ (Sec. 12). In the presence of HCl and other strong acids the dissociation of $H_2C_2O_4$ is rather weak. If a weakly dissociated compound is formed during the reaction, the precipitate must dissolve. On the other hand, acetic acid is weaker than oxalic and therefore cannot suppress the dissociation of the latter to a sufficient extent. The differences in the behaviour of other sparingly soluble salts, such as $BaCrO_4$, $KHC_4H_4O_6$, etc., with HCl and CH_3COOH can be explained similarly.

It is clear from all this that *if we want to dissolve a salt which is sparingly soluble in water, we must act on it with an acid which is stronger than the acid formed in the reaction.*

2. Soluble sulphates (SO_4^{--} ions) give a white precipitate of $CaSO_4$ only with relatively concentrated solutions of calcium salts:

$$Ca^{++} + SO_4^{--} = \downarrow CaSO_4$$

The precipitate is soluble in $(NH_4)_2SO_4$ owing to the formation of a complex salt. In contrast to Ba^{++} and Sr^{++}, calcium salts do not give a turbidity with gypsum water.

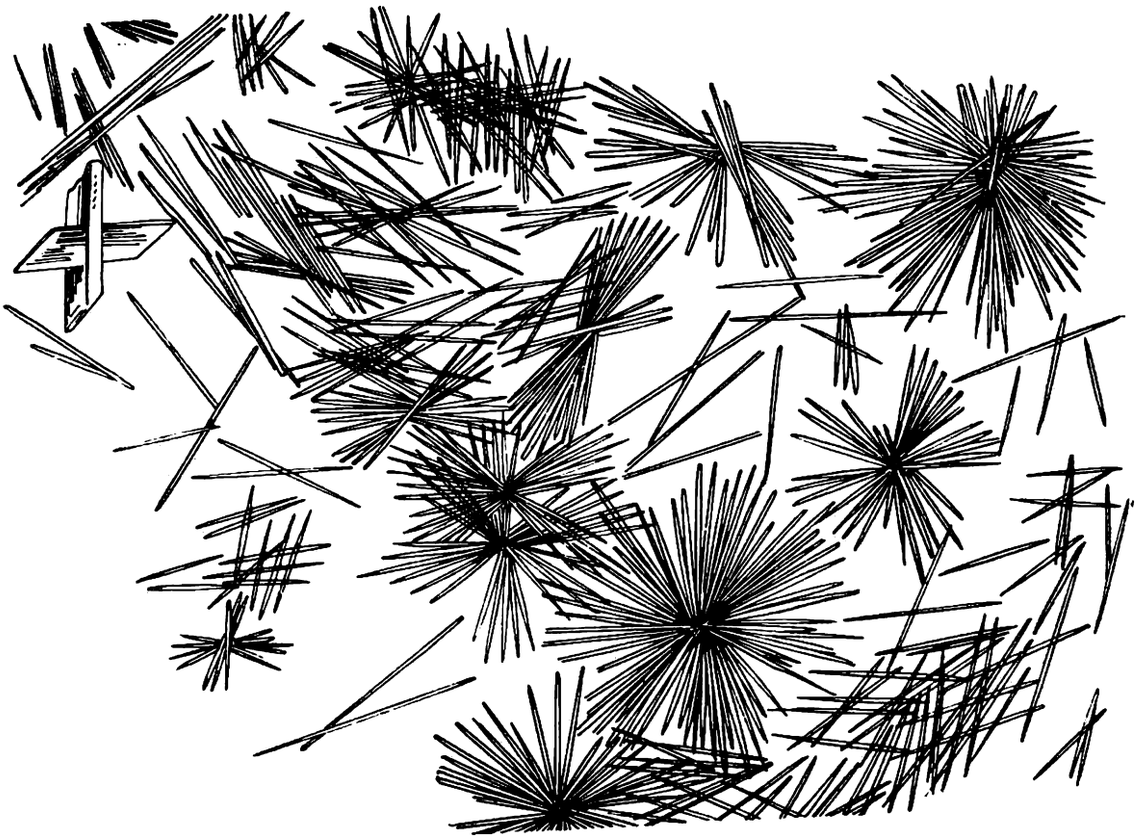


Fig. 23. Crystals of $CaSO_4 \cdot 2H_2O$ formed from dilute solutions

3. Potassium ferrocyanide, $K_4[Fe(CN)_6]$, can be used for detecting Ca^{++} in the presence of Sr^{++} and for separating these ions. The reaction may be represented by the equation

$$CaCl_2 + 2NH_4Cl + K_4[Fe(CN)_6] = Ca(NH_4)_2[Fe(CN)_6] + 4KCl$$

To carry out the test, add a little NH_4Cl and NH_4OH to a solution of a calcium salt, heat to boiling, and add an approximately equal volume of saturated $K_4[Fe(CN)_6]$ solution. A white crystalline precipitate of $Ca(NH_4)_2[Fe(CN)_6]$ is formed, *insoluble in acetic acid.* This distinguishes it from $SrCO_3$, which may form if $(NH_4)_2CO_3$ is present as an impurity in the ammonia used. If present in considerable concentration, Ba^{++} can also give a precipitate with $K_4[Fe(CN)_6]$. Therefore this reaction should not be used for detection of Ca^{++} in the presence of Ba^{++}.

4. Disodium hydrogen phosphate, Na_2HPO_4, forms a white precipitate of $CaHPO_4$ with Ca^{++}:

$$Ca^{++} + HPO_4^{--} = \downarrow CaHPO_4$$

The precipitate is soluble in acids, including acetic.

5. Microcrystalloscopic test. Add a drop of dilute H_2SO_4 solution to a drop of a calcium salt solution on a glass slide and evaporate slightly until a rim appears around the drop. Examine the crystals of gypsum, $CaSO_4 \cdot 2H_2O$, under the microscope. Dependent on the Ca^{++} concentration, their form may be as shown in Fig. 23 or 24.

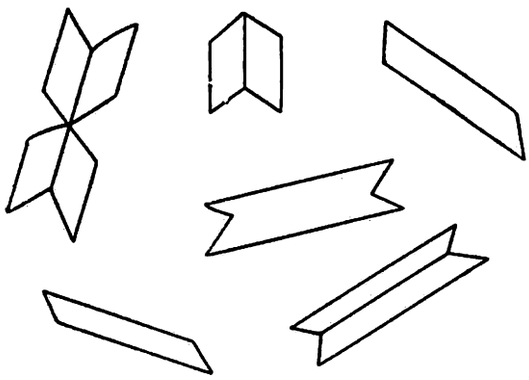


Fig. 24. Crystals of $CaSO_4 \cdot 2H_2O$ formed from relatively concentrated solutions

The reaction detects 0.4 μg Ca^{++}. The dilution limit is 1:25,000. It is usually possible by this test to detect Ca^{++} in the presence of Ba^{++} and Sr^{++}, because barium and strontium sulphates are precipitated in the form of small crystals, easily distinguished from the characteristic large gypsum crystals.

6. Flame test. Volatile calcium salts colour a colourless flame brick-red.

38. Analysis of Mixtures of Group II Cations

The effects of the most important reagents on Group II cations are compared in Table 11.

The table shows that *carbonates, phosphates, oxalates, and sulphates of Group II cations are sparingly soluble in water. Of the chromates,* $BaCrO_4$ *and* $SrCrO_4$ *are sparingly soluble and* $CaCrO_4$ *is readily soluble.* The sulphates are increasingly more soluble in the sequence Ba, Sr, Ca.

With the aid of these reactions several different methods of analyzing a mixture of Group II cations can be devised; only the simplest is considered here. It is discussed in the description given below. Table 12 illustrates it schematically; it demonstrates the separations during the various analytical operations and gives the student a better picture of the course of the analysis as a whole.

Of course, the student must not work merely from the table, without having read carefully the corresponding points in the description of the analytical procedure. This would inevitably lead to errors, as the table gives no indications regarding the conditions and techniques for carrying out the individual operations. Moreover, the individual operations are explained in the description; if they are not understood, the work becomes mechanical.

The description of the analytical procedure and the table allow for the possible presence of Group I cations together with Group II

Table 11

Reactions of Group II Cations

Reagents	Cations		
	Ba++	Sr++	Ca++
$(NH_4)_2CO_3$	White precipitate **$BaCO_3$**	White precipitate **$SrCO_3$**	White precipitate **$CaCO_3$**
Na_2CO_3 and K_2CO_3	$BaCO_3$	$SrCO_3$	$CaCO_3$
Na_2HPO_4	White precipitate $BaHPO_4$	White precipitate $SrHPO_4$	White precipitate $CaHPO_4$
H_2SO_4 and soluble sulphates	White precipitate **$BaSO_4$** insoluble in acids	White precipitate **$SrSO_4$** insoluble in acids	White precipitate * **$CaSO_4$**
$CaSO_4$	White precipitate (turbidity) **$BaSO_4$** formed at once	White precipitate (turbidity) **$SrSO_4$** formed after a delay	—
$(NH_4)_2C_2O_4$	White precipitate BaC_2O_4	White precipitate SrC_2O_4	White precipitate **CaC_2O_4**
K_2CrO_4	Yellow precipitate $BaCrO_4$	Yellow precipitate $SrCrO_4$	—
$K_2Cr_2O_7$ + + CH_3COONa or K_2CrO_4 + + CH_3COOH	Yellow precipitate **$BaCrO_4$**	—	—
$K_4[Fe(CN)_6]$ + + NH_4OH + + NH_4Cl	— **	—	White precipitate $Ca(NH_4)_2[Fe(CN)_6]$
Flame colour	Yellow-green	Crimson	Brick-red

* Precipitate forms only if the solution is not too dilute.

** A precipitate may form at high Ba++ concentrations.

in the "unknown" solution. The solution may also contain a precipitate in which may be present compounds soluble in acids (such as Group II carbonates, oxalates and phosphates, magnesium hydroxide, etc.) as well as the acid-insoluble sulphates of barium, strontium and calcium.

Two variants of the analytical procedure for Groups I and II are given below: (a) in the presence of Sr^{++}, and (b) if strontium is known to be absent.

ANALYSIS OF A MIXTURE OF GROUP I AND II CATIONS

1. Preliminary tests. The analysis is started with preliminary tests on separate portions of the unknown solution. They are as follows.

(a) Determination of the solution pH with the aid of a range of indicators, or a universal indicator (pp. 81-82).

(b) Detection of NH_4^+ by the action of alkali or with Nessler's reagent (Sec. 21, 1 and 2). It will be remembered that NH_4^+ will be later introduced into the solution with the group reagent for Group II, and therefore it must be detected previously in a separate portion of the solution.

Note. If Mg^{++} is present, alkali will precipitate $Mg(OH)_2$. Nessler's solution, which contains alkali, has the same effect (p. 95).

Moreover, in both tests for NH_4^+ the carbonates of Group II are precipitated, because caustic alkalies (NaOH and KOH) usually contain Na_2CO_3 or K_2CO_3 owing to adsorption of CO_2 from the air. The formation of these precipitates does not interfere with detection of NH^+.

(c) Test for sulphates of Group II cations (carried out only if a precipitate is present)*. Shake up the precipitate, transfer 1-2 ml of the turbid liquid to another test tube, and add 2-3 ml of 2 *N* HCl**. If the precipitate does not dissolve, Group II sulphates are present.

2. Dissolving the precipitate and separation of Group II sulphates.

(a) *In the absence of sulphates* dissolve the precipitate in the unknown solution in the least possible amount of 2 *N* HCl, and investigate the solution as described in *4 et seq.*

(b) *In the presence of sulphates* acidify the solution with a few millilitres of 2 *N* HCl to dissolve all the acid-soluble components of the precipitate (such as carbonates, phosphates, etc.). Heat the liquid nearly to boiling, filter off the undissolved residue of $BaSO_4$.

---

* In case a precipitate is absent proceed in accordance with *4 et seq.* after the test for NH_4^+.

** Concentrated HCl cannot be used for this test, as it precipitates chlorides such as $BaCl_2$, NaCl, etc., the solubility of which is lowered by the presence of a large excess of the common Cl^- ion (Sec. 25).

$SrSO_4$ (and $CaSO_4$), and investigate as described in *3.** The filtrate is investigated as described in *4 et seq.*

3. Investigation of the sulphate precipitate. To dissolve barium, strontium and calcium sulphates, they must first be converted into the corresponding carbonates by the action of Na_2CO_3. Filter off the precipitate contained in the unknown solution, remove it from the filter with a spatula, and transfer it to a porcelain basin. Add 15-20 ml of 3 *N* Na_2CO_3 solution and boil for 5-10 minutes. Allow the precipitate to settle, decant the liquid from it, add a fresh portion of Na_2CO_3, and boil again (Sec. 35-2). Filter off the precipitate, *wash it thoroughly* with distilled water to remove the SO_4^{--} ions in solution, and treat on the filter with a few ml of 2 *N* acetic acid. This dissolves the Group II carbonates which were formed, and the Ba^{++}, Sr^{++} and Ca^{++} ions together with excess CH_3COOH pass into the filtrate. This is tested for Ba^{++} and Sr^{++} as described in *7-9*,** or added to the acetic acid solution obtained as described in *6*.

The thorough washing of the precipitate is necessary because otherwise when it is treated with CH_3COOH the SO_4^{--} ions pass into solution together with the Ba^{++} and Sr^{++} ions and precipitate the latter as their sulphates. Usually barium sulphate is not completely converted into the carbonate by twofold treatment with Na_2CO_3, and therefore not all the precipitate dissolves when treated with CH_3COOH. However, this does not matter, because enough Ba^{++} to be detected nevertheless must pass into solution.

Instead of the wet method described here, the sulphates can be converted into carbonates by a dry method, by fusion with a mixture of Na_2CO_3 and K_2CO_3 (p. 165).

4. Test for the presence of Group II cations. Before the systematic analysis of the solution it is necessary to determine whether it contains Group II cations. To a small portion of the solution add a little NH_4Cl and NH_4OH (until the liquid smells of ammonia), and then add $(NH_4)_2CO_3$. A precipitate proves the presence of Group II cations.***

5. Separation of Group II and Group I cations. If Group II cations are present, they must first be separated from Group I, because Ca^{++}, Sr^{++} and Ba^{++} give precipitates with certain reagents used in analysis of Group I (for example, with Na_2HPO_4, $NaHC_4H_4O_6$, etc.).

---

* While Ba^{++} and Sr^{++} are completely precipitated if sufficient SO_4^{--} is present in solution, some Ca^{++} ions always remain in solution because of the appreciable solubility of $CaSO_4$. Therefore when analyzing the sulphate precipitate the Ca^{++} ion need not be detected in it.

** There is no need to test for Ca^{++} in this solution because the solubility of calcium sulphate is appreciable, sufficient for detection of calcium in the solution remaining after separation of the precipitated sulphates.

*** If no precipitate forms (if the solution is alkaline), only Group I cations can be present; for their detection see p. 105 *et seq.*

To the whole solution (in a beaker or flask) add 2 *N* NH_4OH solution until the liquid smells of ammonia, and a little NH_4Cl.* Heat the solution nearly to boiling and add $(NH_4)_2CO_3$ to precipitate Group II cations. Test for complete precipitation by filtering off 1-2 ml of the liquid, adding a little $(NH_4)_2CO_3$ to the filtrate, and warming slightly. If no precipitate or turbidity forms, the precipitation is complete; otherwise more $(NH_4)_2CO_3$ must be added to the whole solution, the latter heated, and the test repeated. When the precipitation is complete, continue heating the liquid with the precipitate gently (not to boiling) until the amorphous precipitate has become crystalline, and is therefore more compact and settled rapidly. Filter it off and wash it once with water.

The precipitate may contain $CaCO_3$, $SrCO_3$ and $BaCO_3$. Investigate it as described in *6 et seq.*; the filtrate, containing Group I cations, is investigated as described on p. 105 *et seq.*

6. Dissolving the precipitated Group II carbonates. Dissolve the washed precipitate in the minimum amount of acetic acid (a strong acid would prevent the subsequent detection of Ba^{++} and Ca^{++}). Put a clean beaker or flask under the funnel and treat the precipitate on the filter with a small amount of dilute (2 *N*) acetic acid, passing the same liquid through the filter two or three times. This solution (to which the acetic acid solution obtained during treatment of the sulphates as described in *3* may be added) is investigated as indicated in *7-10* (in the possible presence of Sr^{++}) or according to *11* if strontium is known to be absent.

7. Detection and separation of Ba^{++}. Test for Ba^{++} in a separate portion of the acetic acid solution with K_2CrO_4 (or with $K_2Cr_2O_7$ in the presence of CH_3COONa). If $BaCrO_4$ is precipitated,** add a little CH_3COONa solution to the whole liquid, heat to boiling, and precipitate Ba^{++} by $K_2Cr_2O_7$ solution added drop by drop until

---

* See Sec. 33 for a discussion of the significance of various factors in precipitation of Group II cations. It must be remembered that too much NH_4Cl should not be added for this precipitation, because this may partially dissolve the carbonates. The amount added should be just sufficient to dissolve the $Mg(OH)_2$ precipitate formed by the action of NH_4OH. Bear in mind, however, that ammonia solution often contains $(NH_4)_2CO_3$ owing to adsorption of atmospheric CO_2. When such a solution is added, Group II carbonates are precipitated together with magnesium hydroxide; these do not dissolve completely in NH_4Cl. Therefore it must first be established by a preliminary test that the ammonia does not give a precipitate with Group II cations, for example with $CaCl_2$ solution, before the disappearance of the precipitate formed by the action of NH_4OH can be used as an indication that enough NH_4Cl has been added. Obviously if the solution had previously been acidified with HCl in the separation of sulphates it is not necessary to add NH_4Cl, because this is formed by the reaction of NH_4OH with HCl.

** If the $BaCrO_4$ precipitate does not form, the solution is tested for the presence of Sr^{++} and Ca^{++} according to *9* and *10*.

the supernatant liquid becomes orange-yellow, indicating an excess of the reagent.

Filter off and discard the precipitate. Investigate the filtrate as described in *8*.

8. Precipitation of Sr^{++} and Ca^{++}. First get rid of the excess potassium dichromate added for precipitation of Ba^{++}, as its colour would interfere with detection of Sr^{++} (or, in its absence, of Ca^{++}). Add Na_2CO_3 until alkaline and heat the liquid. Filter off* the precipitated $CaCO_3$ and $SrCO_3$, wash the precipitate, and dissolve it in dilute acetic acid. Investigate the resultant solution according to *9*.

9. Detection and separation of Sr^{++}. To 1-2 ml of the solution add an equal volume of gypsum water and heat. A white turbidity of $SrSO_4$ forming after some time** indicates the presence of Sr^{++}. If no turbidity appears, allow the liquid to stand for about 10 minutes before concluding that Sr^{++} is absent.

If Sr^{++} is present, precipitate it from the whole solution by adding excess of $(NH_4)_2SO_4$ solution and heating for 10-15 minutes.*** This precipitates Sr^{++} in the form of $SrSO_4$, whereas most of the Ca^{++} remains in solution because its sulphate is soluble in $(NH_4)_2SO_4$. After the precipitate has been filtered off and washed it can be used for confirmatory tests for Sr^{++} (see below). The filtrate is tested for Ca^{++} according to *10*.

The presence of Sr^{++} in the precipitate may be confirmed by the flame test. The precipitate is first washed twice with $(NH_4)_2SO_4$ solution to remove the small amount of $CaSO_4$ which may be present. It is then heated with Na_2CO_3 solution to convert $SrSO_4$ into $SrCO_3$, which is filtered off, washed, and dissolved in a few drops of HCl solution. The resultant $SrCl_2$ solution is then tested in the flame. A crimson colour confirms the presence of Sr^{++}. Alternatively, the $SrCO_3$ precipitate may be dissolved in CH_3COOH and tested for Sr^{++} by the microcrystalloscopic test (p. 167).

10. Detection of Ca^{++}. Add $(NH_4)_2C_2O_4$ to the solution obtained as described in *9*. A white precipitate of CaC_2O_4, insoluble in CH_3COOH but soluble in HCl, indicates the presence of Ca^{++}. For confirmation, a part of the precipitate may be dissolved in HCl and a drop of the solution tested microcrystalloscopically with H_2SO_4 as described on p. 170.

---

* The filtrate, which contains CrO_4^{--} and excess Na_2CO_3, is not investigated.

** If a turbidity appears immediately on addition of $CaSO_4$, this indicates the incomplete separation of Ba^{++}, and the presence or absence of Sr^{++} remains undecided.

*** If the reaction with $K_4[Fe(CN)_6]$ is used for detection of Ca^{++}, it is not necessary to remove Sr^{++}.

11. Analytical procedure in absence of Sr^{++}. When Sr^{++} is known to be absent, first test for Ba^{++} in a separate portion of the solution by the action of K_2CrO_4 solution (or $K_2Cr_2O_7$ in the presence of CH_3COONa). If a yellow precipitate of $BaCrO_4$ is formed, precipitate Ba^{++} from the whole solution (previously heated to boiling) by dropwise addition of hot $(NH_4)_2SO_4$ solution. This precipitates Ba^{++} as $BaSO_4$, while most of the Ca^{++} remains in solution because its sulphate is fairly readily soluble in $(NH_4)_2SO_4$.

Test for complete precipitation, filter off the $BaSO_4$ precipitate, and discard it. Test the filtrate for Ca^{++} as described in *10*.

DETECTION OF GROUP II CATIONS IN SEPARATE PORTIONS OF THE SOLUTION

Appreciable losses of Group II cations occur in the course of systematic analysis, and these cations may be missed as a result. There are several causes of these losses. First, when Group III cations are precipitated by the group reagent, $(NH_4)_2S$, in the presence of NH_4OH the Group II cations may be precipitated as carbonates, because these reagents usually contain $(NH_4)_2CO_3$ formed by adsorption of CO_2 from the air. Further, Ba^{++} and Sr^{++} may also be precipitated owing to oxidation of S^{--} ions to SO_3^{--}, $S_2O_3^{--}$ and SO_4^{--} by atmospheric oxygen. Finally, Group II cations may be coprecipitated with the hydroxides of trivalent Group III cations.

Accordingly, if Group II carbonates are not precipitated by the action of $(NH_4)_2CO_3$ in the course of systematic analysis, Group II cations should be sought in separate portions of the original solution. The following procedure may be used.

1. Detection of Ca^{++}. To 2 ml of the unknown solution, containing any precipitate present in suspended form, add 1 ml of 4 *N* H_2SO_4 solution, followed by 3 ml of ethyl alcohol (or 6 ml of methyl alcohol) to lower the solubility of $CaSO_4$. Rub the walls of the test tube with a glass rod to speed up precipitation of $CaSO_4$. After 3-5 minutes filter off the precipitate and test for complete precipitation. Shake the precipitate for some time with 5-6 ml of water, which dissolves a considerable amount of $CaSO_4$. Filter off the undissolved residue, evaporate 1 ml of the filtrate slightly on a glass slide, and examine under the microscope the crystals formed around the edges. In the presence of Ca^{++} the border consists of long needle-shaped crystals of $CaSO_4 \cdot 2H_2O$, usually in clusters (see Fig. 23).*

---

* As the solubility product of CaC_2O_4 (1.6×10^{-9}) is less than that of $CaSO_4$ (6.1×10^{-5}) the residual solution can also be tested with $(NH_4)_2C_2O_4$. After some time (earlier if rubbed with a glass rod) the solution becomes turbid owing to precipitation of CaC_2O_4. The turbidity does not dissolve when a drop of concentrated acetic acid is added, but is dissolved by HCl.

Table 12

Analysis of a Mixture of Group I and II Cations *

1. Preliminary tests: (a) test for NH_4^+; (b) test for Group II sulphates

2. Dissolve the precipitate and separate Group II sulphates by the action of HCl

Precipitate: $BaSO_4$, $SrSO_4$ ($CaSO_4$)
3. Convert sulphates into carbonates by the action of Na_2CO_3. wash, dissolve in CH_3COOH. Add the liquid to the solution obtained in *6*, or test separately for Ba^{++} and Sr^{++} according to *7-9*

Solution: Cations of Groups II and I (HCl)
4. Test for Group II by $(NH_4)_2CO_3$ in presence of NH_4OH and NH_4Cl

5. Separate Group II cations from the whole solution by the same reagents

Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$
6. Dissolve in CH_3COOH

7. Detect and separate Ba^{++} by $K_2Cr_2O_7$ in presence of CH_3COONa

Precipitate: $BaCrO_4$, not investigated

Solution: Sr^{++}, Ca^{++} ($Cr_2O_7^{--}$)
8. Precipitate Sr^{++} and Ca^{++} by excess Na_2CO_3

Precipitate: $SrCO_3$, $CaCO_3$
9. Dissolve in CH_3COOH, test for Sr^{++} by $CaSO_4$ and separate it by excess $(NH_4)_2SO_4$

Solution: K_2CrO_4 and Na_2CO_3, not investigated

Residue: $SrSO_4$. Confirmatory tests for Sr^{++}

Solution: Ca^{++} [$(NH_4)_2SO_4$]
10. Test for Ca^{++} with $(NH_4)_2C_2O_4$, dissolve in HCl; confirmatory test for Ca^{++}

Solution: Mg^{++}, K^+, Na^+ [$(NH_4)_2CO_3$, NH_4Cl, etc.] Investigate as for Group I (p. 105 *et seq.*)

* The numbers in the table refer to the same operations as in the description of the analytical procedure.

2. Ba^{++} and Sr^{++} may be detected in different ways.

(a) Take 5-10 ml of the unknown solution and add HCl to precipitate the first subgroup of Group IV (p. 367, *2*). Filter and add H_2SO_4 to the filtrate to precipitate $BaSO_4$, $SrSO_4$, $PbSO_4$ and (partially) $CaSO_4$. Test for complete precipitation, filter, wash the precipitate, and heat it with 5-10 ml of 6 *N* NaOH. This dissolves out $PbSO_4$ as lead plumbite, Na_2PbO_2. Filter off and wash the residue, convert the sulphates of barium and strontium into carbonates as described on p. 173 (*3*), dissolve the residue of $BaCO_3$, $SrCO_3$ and possibly $CaCO_3$ in 3-5 ml of 2 *N* acetic acid, and test the solution for Ba^{++} and Sr^{++} by the usual method (Table 12) or by the spot test with sodium rhodizonate (p. 166).

(b) The precipitate of the first subgroup of Group IV may also contain Ba^{++} and Sr^{++} ions.* To avoid detecting them twice, it is advisable when precipitating the first subgroup of Group IV to add enough H_2SO_4 or $(NH_4)_2SO_4$ to precipitate Ba^{++} and Sr^{++} completely. They are then tested for after separation of all the other constituents of the precipitate as described on pp. 367, 370-371. Of course, after $BaSO_4$ and $SrSO_4$ have been converted into carbonates and the latter dissolved in CH_3COOH, the spot test with sodium rhodizonate can also be used to detect Ba^{++} and Sr^{++} (p. 166).

QUESTIONS AND PROBLEMS

1. How does analytical Group II differ from (a) Group I? (b) Groups III, IV and V?
2. In what position of the periodic table are the metals forming the cations of analytical Group II?
3. Explain why $(NH_4)_2CO_3$ is used as the group reagent for Group II rather than Na_2CO_3 or K_2CO_3.
4. For what purpose are (a) NH_4OH and (b) NH_4Cl added in the precipitation of Group II? Explain why too much NH_4Cl must not be added. Why is the solution heated during this precipitation?
5. State the conditions favouring the formation of coarse-grained precipitates.
6. Explain why excessively large or excessively small filters should not be used for filtration.
7. Why are precipitates washed? How should the washing be carried out to make it as rapid as possible?
8. Describe the tests for (a) complete precipitation; (b) complete washing.
9. Why is barium chromate and not the dichromate formed by the action of potassium dichromate on a barium salt? Why is sodium acetate added in this reaction?
10. Explain the difference between the behaviour of $BaCrO_4$ with hydrochloric and acetic acid.

---

* The precipitate of the first subgroup of Group IV cations contains Ba^{++} and Sr^{++} if the unknown solution also contains SO_4^{--}. If not enough of the latter is present for complete precipitation, Ba^{++} and Sr^{++} occur both in the solution and in the precipitate.

11. List all the sparingly soluble salts of barium which you know, indicating the effects of acids on them. Why does $BaSO_4$ differ from all the other barium salts in its behaviour with acids?

12. How can barium sulphate be converted into the carbonate (a) by a dry method? (b) by a wet method? Why is repeated treatment of the precipitate with appropriate reagent necessary in the second case?

13. Find the ratio of CO_3^{--} and SO_4^{--} concentrations at equilibrium when $BaSO_4$ is treated with Na_2CO_3 solution.

Answer.

$$[CO_3^{--}] : [SO_4^{--}] = 73.$$

14. Is it permissible to treat the mass obtained after fusion of $BaSO_4$ with a mixture of sodium and potassium carbonates directly with CH_3COOH, without preliminary boiling with water? Explain your answer.

15. List the sparingly soluble salts of calcium, stating the effects of acids on them.

16. Explain how calcium can be precipitated practically completely by ammonium oxalate from a solution containing HCl without neutralization of the latter.

17. Potassium sulphate is added to a neutral solution of a calcium salt, the precipitate is filtered off, complete precipitation is confirmed, and ammonium oxalate is added to the filtrate. Find, using the solubility products of calcium sulphate and oxalate, whether CaC_2O_4 is precipitated.

18. Explain why the precipitate must be tested with CH_3COOH before testing for Ca^{++} with $K_4[Fe(CN)_6]$.

19. A solution contains cations of Groups II and I. Can the analysis be started (a) by detection of Mg^{++} by the reaction with Na_2HPO_4 and NH_4OH? (b) by detection of Ba^{++} by the action of $K_2Cr_2O_7$? (c) by detection of Ca^{++} by the reaction with $(NH_4)_2C_2O_4$?

20. Why is acetic and not hydrochloric acid used for dissolving the precipitates formed by the group reagent for Group II?

21. In analysis of Group II, $SrSO_4$ was not precipitated immediately after addition of $CaSO_4$ solution. From this it was concluded that Sr^{++} was absent. Is this the only error, or could it lead to further errors?

22. Given a mixture of Group II and I cations, state whether (a) Group II cations, and (b) Group I cations can be found in it without separation of the other group.

23. A mixture of solid salts for analysis contains $CaCl_2$, $BaCl_2$, Na_2CO_3 and K_2SO_4, the last of these being in excess. State what chemical reactions occur when this mixture is dissolved in water, and describe the analytical procedure to be used with it.

CHAPTER IV

CATIONS OF GROUP III

THEORETICAL ASPECTS

39. Precipitation of Sulphides

The classification of cations given in Table 2 (p. 32) shows that, in contrast to Groups I and II, the sulphides of Group III, IV and V cations are practically insoluble in water. This difference is used in systematic analysis for precipitating the last three groups as sulphides by the action of S^{--} ions and thus separating them from the solution. The sulphide ion is the anion of the very weak acid H_2S, which dissociates as follows:

$$H_2S \rightleftarrows H^+ + HS^-$$

$$HS^- \rightleftarrows H^+ + S^{--}$$

Since H_2S is a weak acid, the S^{--} ions introduced into the solution combine with the H^+ ions present to form HS^- ions and undissociated H_2S molecules. Because of this, the S^{--} concentration depends to a very great extent on the H^+ ion concentration, i.e., on the solution pH. The relationship between these concentrations is easily established from the equations for the two dissociation constants of H_2S:

$$K_1 = \frac{[H^+]\cdot[HS^-]}{[H_2S]} = 5.7 \times 10^{-8}$$

$$K_2 = \frac{[H^+]\cdot[S^{--}]}{[HS^-]} = 1.2 \times 10^{-15}$$

Multiplying the two equations together and cancelling $[HS^-]$ from the numerator and denominator, we have

$$\frac{[H^+]^2\cdot[S^{--}]}{[H_2S]} = 6.8 \times 10^{-23} \qquad (1)$$

and

$$[S^{--}] = \frac{6.8 \times 10^{-23} \times [H_2S]}{[H^+]^2} \qquad (2)$$

Equation (2) shows that *the* S^{--} *ion concentration is inversely proportional to the square of the* H^+ *ion concentration in solution.* For example, if the pH is lowered by one unit, i.e., if $[H^+]$ is increased tenfold, the S^{--} concentration decreases a hundredfold. It follows that in a solution with $[H^+] = 10^{-1}$, i.e., pH = 1, the S^{--} con-

centration must be less by a factor of $(10^8)^2 = 10^{16}$ than in a solution where $[H^+] = 10^{-9}$ or pH = 9.

Accordingly, the pH of the solution determines to a very great extent whether a particular sulphide is precipitated or not, and the degree to which it may be precipitated.

For example, at low pH values, i.e., in acid solutions, only sulphides with very small solubility products can be precipitated, as the very low S^{--} concentrations existing in acid solutions are sufficient only to exceed their values. Conversely, in neutral or alkaline solutions sulphides with much larger solubility products are precipitated as well as these least soluble sulphides. It is evident that cations may be separated by suitable regulation of the solution pH during precipitation by S^{--} ions.

This is the principle on which the separation of Groups IV and V from Group III and the precipitation of Group III is based. Leaving aside Group V for the moment (the separation of this group will be considered in Sec. 75), let us compare the solubility products of certain sulphides of Group III and IV cations:

	Group III	*Group IV*
Most soluble sulphides	$SP_{MnS} = 1.4 \times 10^{-15}$	$SP_{CdS} = 3.6 \times 10^{-29}$
Least soluble sulphides	$SP_{ZnS} = 1.2 \times 10^{-23}$	$SP_{CuS} = 8.5 \times 10^{-45}$

These figures show that *Group IV sulphides are much less soluble than Group III sulphides, and therefore may be precipitated at lower* pH *values, i.e., in solutions of higher acidity.*

We now pass from qualitative conclusions to quantitative calculation of the pH values required for separation of these groups and for separating them from Groups II and I.

First we calculate the pH at which the Group IV sulphides are completely precipitated. For this it is sufficient to find the pH needed for complete precipitation of CdS, because all the other Group IV sulphides are less soluble and should be precipitated even more completely when the precipitation of CdS is fairly complete. If hydrogen sulphide is passed through the solution to effect the precipitation, the H_2S concentration is equal to its solubility, about 1×10^{-1} *M* at room temperature.

Therefore from Eq. (1) we find

$$[H^+]^2 \times [S^{--}] = 6.8 \times 10^{-23} \times [H_2S] = 6.8 \times 10^{-24} \tag{3}$$

Solving Eq. (3) for $[H^+]$, we have

$$[H^+] = \sqrt{\frac{6.8 \times 10^{-24}}{[S^{--}]}} \tag{4}$$

On the other hand if, as previously, we take the precipitation as complete when the concentration of the precipitated ion (Cd^{++}) has fallen to 10^{-6} g-ion/litre, we can write:

$$[S^{--}]=\frac{SP_{CdS}}{[Cd^{++}]}=\frac{3.6\times 10^{-29}}{10^{-6}}=3.6\times 10^{-23}\ \text{g-ion/litre}$$

Substituting the value found for $[S^{--}]$ into Eq. (4), we have

$$[H^+]=\sqrt{\frac{6.8\times 10^{-24}}{3.6\times 10^{-23}}}=0.44\ \text{g-ion/litre}$$

This value for $[H^+]$ corresponds to

$$pH=\log 0.44=\bar{1}.64=1-0.64=0.36$$

Thus, the precipitation of Cd^{++} and therefore of all the other Group IV cations is complete at $pH \geqslant 0.36$. As the reaction with H_2S liberates H^+ ions, which gradually lower the pH, in practice the precipitation is started at a somewhat higher pH, namely 0.5, corresponding to $[H^+] = 0.3$ g-ion/litre.

Under these conditions all the Group III cations remain in solution, as is evident from the following calculation.

Let the Zn^{++} ion concentration in our solution be 1×10^{-1} g-ion/litre. The S^{--} concentration at $[H^+] = 0.3$ g-ion/litre is

$$[S^{--}]=\frac{6.8\times 10^{-24}}{0.3^2}=8\times 10^{-23}\ \text{g-ion/litre}$$

Therefore the ionic product is

$$[Zn^{++}]\cdot[S^{--}]=10^{-1}\times 8\times 10^{-23}=8\times 10^{-24}$$

Since this is less than the solubility product of zinc sulphide ($1.2 \times \times 10^{-23}$), it follows that ZnS and therefore all the other (more soluble) sulphides of Group III are not precipitated by hydrogen sulphide at $pH = 0.5$. Of course, the cations of Groups II and I, the sulphides of which are soluble in water, are not precipitated either. Therefore *at* $pH = 0.5$ *Group IV cations can be separated from Groups III, II and I by the action of* H_2S.

The sulphides of Group III cations are then precipitated from the filtrate obtained after separation of the Group IV cations. Let us calculate the pH at which this must be carried out. Group III cations may be precipitated either by H_2S or by $(NH_4)_2S$. In the former case the calculation is exactly the same as for precipitation of Group IV sulphides, except that in this case we have to start with the solubility product of the most soluble sulphide in Group III, namely, manganese sulphide ($SP = 1.4 \times 10^{-15}$). Assuming that the precipitation of the Group III cations is complete when the Mn^{++} concen-

tration has fallen to 10^{-6} g-ion/litre, we find the required S^{--} ion concentration:

$$[S^{--}]=\frac{SP_{MnS}}{[Mn^{++}]}=\frac{1.4\times 10^{-15}}{10^{-6}}=1.4\times 10^{-9}\ \text{g-ion/litre}$$

Hence, using Eq. (4), we have

$$[H^+]=\sqrt{\frac{6.8\times 10^{-24}}{[S^{--}]}}=\sqrt{\frac{6.8\times 10^{-24}}{1.4\times 10^{-9}}}=7\times 10^{-8}\ \text{g-ion/litre}$$

Consequently

$$pH=-\log 7\times 10^{-8}=-(0.8-8)=7.2$$

Thus, Group III cations are completely precipitated by hydrogen sulphide even in a practically neutral solution (pH = 7.2). However, this does not mean that Group III cations can be precipitated by passing hydrogen sulphide through a solution not containing free acid. It must be remembered that solutions of Group III salts have an acid reaction even without acidification, owing to hydrolysis.

Moreover, hydrogen sulphide acts as an acid when dissolved in water, and lowers its pH to about 4. Therefore, in contrast to Group IV, the sulphides of Group III are usually not precipitated when hydrogen sulphide is passed through the unknown solution. Even if a precipitate does form sometimes (in the case of ZnS), the precipitation is very incomplete because of formation of H^+ ions in the solution:

$$Zn^{++}+H_2S \rightleftarrows \downarrow ZnS+2H^+$$

Therefore for complete precipitation of all the Group III cations by the action of H_2S *we must first add a buffer mixture maintaining the* pH *practically constant at or above* 7.2. Of the usual buffers (see p. 78) only the ammonium buffer mixture with pH $\approx$ 8-9 is suitable in this case.

Instead of H_2S, it is more usual to precipitate Group III by *ammonium sulphide solution*, $(NH_4)_2S$, *which is the group reagent for Group III.*

As in the separation of Group II cations (Sec. 33), the pH required for precipitation of Group III by ammonium sulphide is largely predetermined by the fact that $(NH_4)_2S$ is hydrolyzed almost completely* in solution:

$$(NH_4)_2S+H_2O \rightleftarrows NH_4HS+NH_4OH$$

Therefore a solution of $(NH_4)_2S$ is really a mixture of equivalent amounts of ammonia and the ammonium salt NH_4HS, i.e., like $(NH_4)_2CO_3$ solution, it is itself an ammonium buffer mixture with

* The mathematical basis for this is given in detail on p. 213, Example 1.

pH = 9.25. Let us now find how complete the precipitation of Group III cations is at this pH. The corresponding H^+ concentration is $5.6 \times \times 10^{-10}$ g-ion/litre. Suppose that the excess of $(NH_4)_2S$ in solution is 0.1 *M*; since this salt is hydrolyzed almost completely to give NH_4HS, we can write $[HS^-] = 0.1$ g-ion/litre. Substituting these values of $[H^+]$ and $[HS^-]$ into the equation for K_2 of hydrogen sulphide, we have:

$$K_2 = \frac{[H^+][S^{--}]}{[HS^-]} = \frac{5.6 \times 10^{-10} \times [S^{--}]}{10^{-1}} = 1.2 \times 10^{-15}$$

and hence

$$[S^{--}] = 2.2 \times 10^{-7} \text{ g-ion/litre}$$

We now find the concentration of Mn^{++} ions remaining in solution after the precipitation:

$$[Mn^{++}] = \frac{SP_{MnS}}{[S^{--}]} = \frac{1.4 \times 10^{-15}}{2.2 \times 10^{-7}} = 1.2 \times 10^{-8} \text{ g-ion/litre}$$

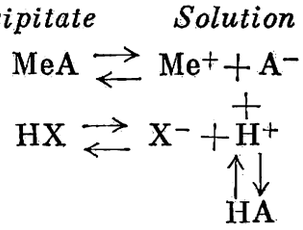
Therefore the precipitation of Mn^{++} is practically complete. As the solubility products of the remaining Group III sulphides are even lower than that of MnS, these sulphides should be precipitated even more completely at this pH.* Therefore we see that *the separation of Groups III and IV, and the separation of Group III from Groups I and II, depends on the different solubility products of the sulphides formed by the cations of these groups, and is effected by appropriate regulation of the solution* pH.

40. Action of Acids on Sulphides

The differences in the behaviour of Group III and IV sulphides with acids, of great importance in analysis, also depend on these same differences between their solubility products.

It was explained in Sec. 28 that in order to dissolve a precipitate we must bind one of the ions which it gives up to the solution. In the case of precipitated salts this is usually effected by the action of acids, the hydrogen ions of which combine with the salt anions to give the corresponding weak (slightly dissociated) acids.

If we represent a salt of a weak acid by the formula MeA, and that of the acid dissolving it by HX, the processes taking place when the precipitated salt is dissolved can be schematically represented as follows:



* The conditions for precipitation of Group III by the group reagent are considered in greater detail in Sec. 52.

The weak acid HA formed in the reaction dissociates, even though only slightly, and yields the same A^- anions which were removed during dissolution of the precipitate. Therefore the process is reversible and ultimately reaches equilibrium. Equilibrium evidently becomes established when the anion concentration $[A^-]$ satisfies two equations simultaneously:

$$[Me^+]\cdot[A^-]=SP_{MeA} \tag{1}$$

$$\frac{[H^+]\cdot[A^-]}{[HA]}=K_{HA} \tag{2}$$

Solving Eq. (1) for $[A^-]$ and substituting the result into Eq. (2), we have

$$[Me^+]\cdot[HA]=\frac{[H^+]\cdot SP_{MeA}}{K_{HA}} \tag{3}$$

But the ionic equation for the reaction

$$MeA + H^+ \rightleftarrows Me^+ + HA$$

shows that when 1 mole of the MeA precipitate dissolves, one gram-ion of Me^+ and one mole of HA appear in the solution. Therefore, denoting the solubility of the precipitate in the acid by P (in moles per litre), we can write

$$P=[Me^+]=[HA]$$

Accordingly, Eq. (3) gives

$$P=\sqrt{\frac{[H^+]\cdot SP_{MeA}}{K_{HA}}} \tag{4}$$

It follows from Eq. (4) that *the solubilities of sparingly soluble salts in acids must increase with (a) increasing solubility product of the salt; (b) decreasing dissociation constant of the weak acid* HA *formed; (c) increasing* H^+ *ion concentration in solution (i.e., decreasing* pH).

These relationships apply to all sparingly soluble salts, including sulphides. If sulphides of Group III and IV cations are treated with the acid taken in the same concentration, the reaction product in each case is the same weakly dissociated compound (H_2S); the difference in the behaviour of the sulphides can be attributed only to differences in their solubility products. Since the solubility products of Group IV sulphides (Sec. 39) are much lower than those of Group III sulphides, it is to be expected that the former are much less easily soluble in acids. In fact, *whereas Group III sulphides dissolve readily in dilute acids* (HCl *and* H_2SO_4), *Group IV sulphides are practically insoluble in them.* Evidently, Group IV sulphides yield so few S^{--} ions into the solution that equilibrium becomes established when only very

small amounts of H_2S have been formed, i.e., when a negligible amount of sulphide has dissolved. On the other hand, the solubility products of Group III sulphides are very much larger, so that in this case more H_2S is formed and if sufficient acid is present the entire precipitate dissolves; this is also assisted by the removal of H_2S in gaseous form. This explanation is fully confirmed by calculation.

Calculations of the solubilities of sulphides in acids are complicated by the fact that hydrogen sulphide dissociates in stages. The reverse process of combination of S^{--} ions with H^+ ions during the dissolution of sulphides in acids is also stepwise in character: HS^- ions are formed first, and these then add further H^+ ions with partial formation of undissociated H_2S molecules. If the formation of both reaction products (HS^- and H_2S) is taken into account, a fourth-power equation, not easy to solve, is obtained in the calculation of sulphide solubilities in acids. However, mathematical investigation shows that if the solubility product of the precipitate is small while K_1 of the corresponding weak acid is very much larger than K_2 (as in the present instance), it may be assumed without appreciable error that all the HS^- ions are converted almost completely into H_2S, i.e., that the reaction is

$$MeS + 2H^+ \rightleftarrows Me^{++} + H_2S$$

With this assumption the solubility of the sulphide can be calculated from the equation

$$\frac{[H^+]^2 \cdot [S^{--}]}{[H_2S]} = K_{H_2S}$$

or

$$[H_2S] = \frac{[H^+]^2 \cdot [S^{--}]}{K_{H_2S}} \qquad (5)$$

where

$$K_{H_2S} = K_1 \times K_2 = 6.8 \times 10^{-23} \text{ (see Sec. 39)}$$

But the concentrations of the S^{--} anions and the Me^{++} cations are connected by the equation

$$[Me^{++}] \cdot [S^{--}] = SP_{MeS}$$

Solving this equation for $[S^{--}]$ and substituting the result into Eq. (5), we have

$$[Me^{++}] \cdot [H_2S] = \frac{[H^+]^2 \cdot SP_{MeS}}{K_{H_2S}} \qquad (6)$$

The reaction equation

$$MeS + 2H^+ = Me^{++} + H_2S$$

shows that two gram-ions of H^+ (i.e., two moles of a strong acid of the HCl type) are required to dissolve one mole of the MeS precipitate, to give one gram-ion of Me^{++} and one mole of H_2S. Therefore, denoting the initial concentration of the solvent acid by c, we can write*

$$P = [Me^{++}] = [H_2S] \text{ and } [H^+] = c - 2P$$

---

* Volatilization of H_2S is neglected here; this is permissible if the acid concentration is such that at equilibrium the solution is not saturated with H_2S (i.e., if less than 0.1 mole/litre of the latter is formed).

Substituting the values of $[Me^{++}]$, $[H_2S]$ and $[H^+]$ into Eq. (6), we have:

$$P^2 = (c-2P)^2 \cdot \frac{SP_{MeS}}{K_{H_2S}}$$

Taking square roots of both sides of the equation and solving for P, we have:

$$P = \frac{c\sqrt{\frac{SP_{MeS}}{K_{H_2S}}}}{2\sqrt{\frac{SP_{MeS}}{K_{H_2S}}}+1}$$

We then divide the top and bottom of the right-hand side of the equation by $\sqrt{\frac{SP_{MeS}}{K_{H_2S}}}$, finally obtaining

$$P = \frac{c}{2+\sqrt{\frac{K_{H_2S}}{SP_{MeS}}}} \qquad (7)$$

The following conclusions may be drawn from Eq. (7).

1. If the solubility product of MeS is large by comparison with K_{H_2S} (which is the case for most of the Group III sulphides), the quantity under the root sign is small. In that case the solubility of the sulphide approaches the maximum value of $c/2$, corresponding to the reaction equation*.

2. Conversely, if the solubility product of MeS is small by comparison with K_{H_2S}, as for the Group IV sulphides, the denominator of the fraction in the right-hand side of the equation is large and P is very small.

This is illustrated by Table 13, which gives the results of calculations from Eq. (7).

Table 13 shows that although Eq. (7) is only approximate, the calculated results are in full *qualitative* agreement with experimental data. Table 13 gives a clear illustration of the influence of the solubility products of sulphides on their solubilities in HCl.

If the calculation of the solubility of a sulphide in an acid is based on the H^+ ion concentration at equilibrium rather than on the initial acid concentration, the following equation (derived by A. K. Babko) is obtained:

$$P = \sqrt{SP_{MeA}\left(\frac{[H^+]}{K_1}+1+\frac{[H^+]^2}{K_1 \cdot K_2}\right)} \qquad (8)$$

The stepwise binding of S^{--} ions by H^+ ions was taken into account in its derivation. However, this equation is not exact either, because activity coefficients of the ions were not taken into account. Moreover, it is difficult to use because often the equilibrium H^+ ion concentration is also unknown, like the required solubility of the sulphide.

Relationships similar to those discussed above apply to other sparingly soluble electrolytes as well as to sulphides. For example,

---

* As 2 moles of HCl is needed to dissolve one mole of MeS, c moles of acid if 100% utilized would dissolve $c/2$ moles of sulphide.

it was stated in Sec. 28 that the hydroxides of magnesium ($SP = 5 \times 10^{-12}$), manganese ($SP = 4 \times 10^{-14}$), ferrous iron ($SP = 4.8 \times 10^{-16}$), etc., are readily soluble in ammonium salts owing to the formation of the weak base NH_4OH. However, $Fe(OH)_3$ ($SP = 3.8 \times 10^{-38}$) and the hydroxides of aluminium and chromium, having very small solubility products, are insoluble in ammonium salts. This fact is used in analysis for separating the Group III cations into two subgroups.

Table 13

Solubilities of Certain Sulphides in 0.1 *N* HCl
[calculated from Eq. (7)]

Formula of sulphide	Solubility product *	Solubility of sulphide, *P*	
		moles/litre	% of maximum solubility (c/2)
MnS	1.4×10^{-15}	5×10^{-2}	100
FeS	3.7×10^{-19}	4.97×10^{-2}	99.4
ZnS	1.2×10^{-23}	2.28×10^{-2}	45.6
NiS_α	3×10^{-21}	4.65×10^{-2}	93.0
NiS_γ	2×10^{-28}	7×10^{-4}	1.4
CoS_α	7×10^{-23}	3.3×10^{-2}	66.0
CoS_β	2×10^{-27}	5.4×10^{-4}	1.1
CdS	3.6×10^{-29}	7.2×10^{-5}	0.14
PbS	1.1×10^{-29}	4.0×10^{-5}	0.08
CuS	8.5×10^{-45}	1.1×10^{-12}	2.10

* The values of *P* and *SP* for the sulphides of nickel and cobalt are given both for the more soluble forms (NiS_α and CoS_α) and for the less soluble forms (NiS_γ and CoS_β). See Appendix IV.

However, if a hydroxide is treated with an acid instead of an ammonium salt it dissolves easily, because H_2O is formed in the reaction and this dissociates much less than NH_4OH. Evidently in this case the result depends on the different dissociation constants of the reaction products.

Sulphides also behave differently with different solvents. For example, the Group IV sulphides are insoluble in HCl but dissolve easily when heated with HNO_3, which oxidizes S^{--} ions as follows:

$$3S^{--} + 2NO_3^- + 8H^+ \rightleftarrows \downarrow 3S + \uparrow 2NO + 4H_2O$$

The equilibrium constant of this reaction is very small. Therefore S^{--} ions are oxidized even when present in concentrations at which

they are no longer removed by combining with H^+ ions. Consequently the effects of HCl and HNO_3 on Group IV sulphides are different because of the different equilibrium constants of the reactions leading to removal of S^{--} ions.

We have already met more than once the influence of H^+ ion concentration on the solubility of precipitates in acids. For example, we saw that precipitates of $KHC_4H_4O_6$, $BaCrO_4$, CaC_2O_4, readily soluble in strong (mineral) acids, are almost insoluble in a weak acid (acetic), which gives a much lower H^+ ion concentration. Similar effects will be met later.

It should be pointed out that this factor has an influence in practice only when the solubility product of the precipitate is relatively small or when K_{HA} is large. For example, unlike $BaCrO_4$ ($SP = 2.4 \times 10^{-10}$), $SrCrO_4$ ($SP = 3.6 \times \times 10^{-5}$) is soluble in acetic acid as well as in strong acids. Similarly, although their solubility products are similar, calcium oxalate (CaC_2O_4) does not dissolve in acetic acid while calcium carbonate, $CaCO_3$, dissolves readily in it, because the dissociation constants of carbonic acids are considerably less than those of oxalic acid.

41. Colloidal Systems

To complete our study of the precipitation process, we must consider the formation of colloidal solutions, which is a complication frequently arising in this highly important analytical operation. Because of the formation of such solutions, certain sparingly soluble substances (e.g., Group III sulphides) cannot be separated from the solution by filtration. The purpose of the whole operation—ion separation—is therefore not achieved.

To avoid this, certain measures have to be taken to prevent the formation of colloidal solutions or to break them down if they form. In order to explain these measures, we must review the nature of colloidal solutions and their most important properties (in relation to analytical chemistry).

If minute particles of a substance are uniformly distributed in some other substance, a *disperse system* is obtained. The fine particles in this system are collectively known as the *disperse phase*, and the substance in which they are distributed is the *dispersion medium*. Disperse systems differ among themselves primarily in the *degree of dispersion* or particle size. The smaller the particles, the higher is the degree of dispersion, and *vice versa*. If the particles of the disperse phase are larger than 100 mμ*, the disperse system is known as a *suspension* if the particles are solid and an *emulsion* if they are liquid. Water containing suspended clay particles is

* It will be remembered that mμ is the symbol for the millimicron or 0.000001 mm, and therefore 100 mμ is equal to 0.0001 mm.

an example of a suspension; an example of an emulsion is milk, which contains minute fat particles in a suspended state.

Disperse systems containing particles between 100 and 1 mμ in size are known as *colloidal solutions* or *sols*,* and if the particles are smaller than 1 mμ they are termed *true solutions*, or simply solutions.

The dispersed particles in true solutions are individual molecules or ions of the dissolved substances. They are too small to be visible with any available magnification. Therefore such solutions are completely homogeneous. On the other hand, suspensions and emulsions, and also colloidal solutions (in which the dispersed particles usually consist of numerous molecules)**, exhibit distinct heterogeneity. For example, the first sign of the heterogeneity of suspensions and emulsions is that they are opaque or turbid. The heterogeneity is even more apparent when suspensions and emulsions are examined under the microscope, when individual dispersed particles may be seen.

Particles in colloidal solutions (smaller than the particles in suspensions or emulsions) cannot be seen under the ordinary microscope. However, in most cases they can be detected with the aid of the *ultramicroscope*. In the ultramicroscope the object is illuminated from the side, and not from below as in the ordinary microscope, so that the light rays do not reach the observer's eye directly and the field appears dark. When a colloidal solution is viewed under the ultramicroscope the dispersed particles scatter the incident light and become visible. They are seen as small bright spots in continuous random movement (Brownian movement).

Colloidal particles readily pass through the pores of ordinary paper or clay filters (through which the larger particles in suspensions and emulsions cannot pass). Therefore the disperse phase of a colloidal solution cannot be separated from the dispersion medium by means of these filters. However, membranes are known having pores so small that even the dispersed particles in colloidal solutions cannot pass through them. Colloidon, parchment or celluloid membranes are examples. Smaller particles (molecules or ions) of solutes in true solutions can pass even through these membranes.

---

* Strictly speaking, it is not quite correct to regard these disperse systems as colloidal solutions. The reason is that in the modern view only thermodynamically stable disperse systems are classed as solutions; as will be shown, sols are more or less unstable systems. However, as the term is in common usage, we shall use it together with the term "sol".

** The molecules of polymeric substances such as proteins, starch, etc., are so large that solutions of these substances have all the properties of colloidal systems. Therefore in such cases the colloidal particles are individual polymer molecules.

Colloidal solutions can be obtained by subdividing (for example, with the aid of special "colloid mills") larger particles down to colloid size.

Instead of these *dispersion* methods for obtaining colloidal solutions, it is possible to use *condensation* methods, in which colloidal particles are formed by cohesion of individual molecules or ions of a substance. This may occur in chemical reactions leading to the formation of sparingly soluble substances. If the experimental conditions are chosen so that particle growth ceases when the particle size has reached the value indicated above (1-100 mμ), a colloidal solution is obtained instead of a precipitate.*

It was originally thought that colloidal solutions could be formed only by a certain class of substances, termed colloids, in contrast to crystalloids unable to form such solutions. However, it has since been shown that even typical crystalloids such as NaCl can form colloidal solutions under suitable conditions. Therefore we now speak of the colloidal and crystalline states of substances rather than of colloids and crystalloids as distinct classes.

A colloidal solution is stable only if its dispersed particles do not join into larger aggregates which settle rapidly under gravity. However, forces exist in colloidal solutions which tend to favour such growth, such as forces of molecular attraction, which may cause the particles to join when they collide. Surface tension of the liquid, which tends to decrease the surface of contact between the liquid and the particles to a minimum, acts in the same direction; for a given total volume of the particles their total surface area decreases with increase of particle size.

This is easy to show by a simple calculation. A cube of 1 cm edge has a surface area of 6 cm^2. If it is subdivided into cubes of 0.1 cm edge, their total area (10^3 cubes) is $6 \times 0.1^2 \times 10^3 = 60$ cm^2, or 10 times as large as before. With cubes of colloidal size, having edges of 0.0001 mm or 0.00001 cm, the total surface area is 600,000 cm^2.

Despite all this, typical colloidal solutions may remain without forming a precipitate for a very long time. This clearly shows that there must be certain factors preventing cohesion of the colloidal particles.

One such factor is the presence of like electric charges on the colloidal particles; these cause mutual repulsion of the particles, which are prevented from joining into larger aggregates.

The existence of these charges can be easily shown when an electric current is passed through a colloidal solution. Some colloidal particles, such as those in colloidal solutions of metals and metal

* One such condition, for example, is a sufficiently low concentration of the reacting substances in solution.

sulphides, move towards the anode, i.e., they are negatively charged. Others, such as colloidal solutions of metal hydroxides, move towards the cathode and are therefore positively charged.

In most cases the charges in colloidal particles arise as the result of adsorption of ions by the particles from solution, usually ions containing one of the elements present in the particles. For example, when a sol of arsenious sulphide is formed by the action of H_2S on the solution of an arsenite (a salt of arsenious acid, H_3AsO_3), particles each consisting of a large number (m) of As_2S_3 molecules are formed. These particles adsorb a certain number (n) of HS^- anions from the solution and thus acquire a negative charge. These negatively charged particles attract the corresponding number (n) of positively charged H^+ ions ("gegenions") from the solution; some of them (x) remain in the liquid phase near the particle to form the so-called diffuse layer while the rest ($n-x$) are adsorbed by the particle surface and move together with the particle. Accordingly, the structure of arsenious sulphide micelles (electrically charged colloidal particles together with the H^+ gegenions of the diffuse layer, neutralizing them electrically) may be schematically represented as follows:

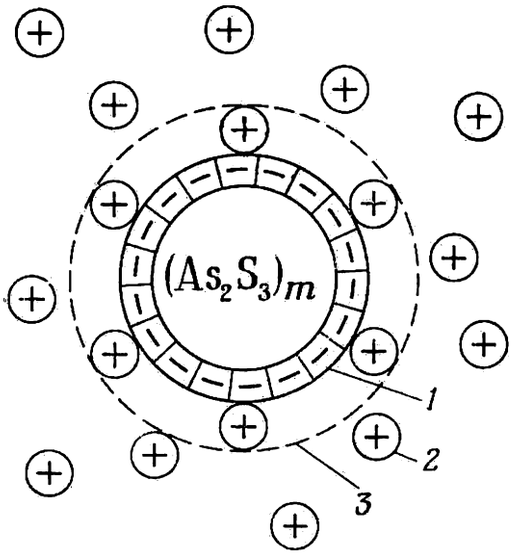


Fig. 25. The As_2S_3 micelle
1—HS^- ion; *2*—H^+ ion; *3*—boundary between the particle and the diffuse layer of gegenions

$$\overbrace{\underbrace{\{(As_2S_3)_m n HS^-}_{\text{Nucleus}},\ (n-x)H^+\}}^{\text{Particle}}\ xH^+$$

Micelle

The structure of the As_2S_3 micelle is also shown in Fig. 25. Similarly, AgI micelles formed in a solution containing a slight excess of KI have the following structure:

$$\{(AgI)_m n I^-,\ (n-x)K^+\}\,xK^+$$

If the same sol is formed in the presence of excess $AgNO_3$, the micelles are represented by the following formula:

$$\{(AgI)_m n Ag^+,\ (n-x)NO_3^-\}\,xNO_3^-$$

In both cases the nucleus of the $(AgI)_m$ micelle has the same chemi-

cal composition and crystalline structure, but the particle charges are different, because they are due to the adsorption of excess I^- ions in the first case, and of excess Ag^+ ions in the second. Substances which confer stability on colloidal solutions owing to adsorption of their ions by the colloidal particles are known as *stabilizers*. In the cases discussed above the stabilizers are H_2S, KI and $AgNO_3$.

It is clear from all this that the formation of a stable colloidal solution requires not only a suitable degree of dispersion of the particles but also the presence of a stabilizer to prevent the colloidal particles from joining into larger aggregates.

In addition to the electric charges of the particles, another stabilizing factor in colloidal solutions is *solvation* (hydration) of the colloidal particles, i.e., adsorption of solvent molecules by them. As a result, the colloidal particles become surrounded by solvate layers which prevent close approach between the particles and consequent formation of larger aggregates. Different colloidal particles differ very considerably in their tendency to undergo solvation. Accordingly, a distinction is made between *lyophilic* and *lyophobic* colloids* (in particular, if water is the solvent the corresponding terms are *hydrophilic* and *hydrophobic*).

While lyophilic colloids have high solvent affinity and are strongly solvated, lyophobic colloids do not in themselves exhibit any appreciable affinity towards the solvent. However, even here some solvation of the particles occurs, although it is much weaker. It is due in this case to the tendency of the ions adsorbed by the particles to surround themselves with solvate layers; this, in addition to the particle charge, is a stabilizing factor for lyophobic sols.

Solutions of proteins, glue, starch and similar substances are hydrophilic colloids; hydrophobic colloids include sols of metals, sulphides, and various salts. Metal hydroxide sols occupy an intermediate position between the two classes.

If a small amount of an electrolyte is added to a hydrophobic colloid sol, the colloidal particles join into larger aggregates and the degree of dispersion of the colloid decreases. If this process, known as *coagulation*, goes far enough, *sedimentation* also occurs and the resultant aggregates sink to the bottom of the vessel under gravity. The coagulation effect is explained most simply with the assumption that the colloidal particles adsorb oppositely charged ions of the

---

* These terms mean "solvent-loving" and "solvent-hating" respectively. It must be pointed out that the terms "lyophilic" and "lyophobic" are not quite correct, because lyophobic colloids also exhibit (although to a lesser degree) the characteristic sign of a lyophilic character—solvation of the dispersed particles. In this case the formation of solvate layers is due to the solvation not of the particles themselves but of the substances (ions) adsorbed by the colloids.

coagulant electrolyte and their charge is thereby decreased so much that they can join together (this is also aided by the accompanying breakdown of the solvate layers). However, coagulation is a very complex phenomenon, and this "adsorption theory" does not give a fully satisfactory explanation of all the diversity of experimental facts. Other and more complex theories have been put forward; these are discussed fully in textbooks of colloid chemistry. However, none is completely exhaustive. Because of this, and of the complexity of many of the theories which have been advanced, in a first study of colloidal solutions we may (for the sake of simplicity) use the concepts of the adsorption theory of coagulation.

In full agreement with this theory, *the coagulating effects of electrolytes increase rapidly with increasing valency of the ions bearing charges of the opposite sign to the colloidal particles.*

For example, in the case of As_2S_3 sol *the coagulating concentrations* (i.e., the minimum concentrations causing coagulation of the given sol) of Al^{+++}, Ba^{++} and K^+ ions are in the ratio of 1 : 20 : 1,000. In the case of $Fe(OH)_3$ sol, the particles of which are positively charged, the valency of the anion of the coagulant electrolyte is significant. For example, the coagulating action increases rapidly in the series Cl^-, SO_4^{--}, $[Fe(CN)_6]^{---}$.

Coagulation may also occur if a solution contains colloidal particles bearing opposing charges, e.g., when an $Fe(OH)_3$ sol is mixed with an As_2S_3 sol, etc.

The most important stability factor in the case of lyophilic colloids is the existence of solvate layers around the particles. Therefore these layers must first be destroyed to induce coagulation of lyophilic colloid sols. This destruction can be achieved by addition of electrolytes, but the concentrations needed are much higher than for lyophobic colloids. At high concentrations the electrolyte ions take solvent molecules from the colloidal particles when undergoing hydration, and thus confer the properties of lyophobic colloid particles on them. The electrolyte ions also discharge the particles, so that the colloid is coagulated; in this case the effect is known as *salting-out.*

The addition of a lyophilic colloid to a lyophobic colloid sol greatly increases the stability of the latter to the action of electrolytes. This effect is known as *colloidal protection*; it depends on adsorption of the lyophilic colloid by the lyophobic particles, which thus acquire solvate layers.

The following example illustrates colloidal protection. If a *protective colloid* (gelatin) is added to $AgNO_3$ solution, followed by HCl, the usual curdy precipitate of AgCl does not form. A turbid opalescent liquid, an AgCl sol, is formed instead. This sol does not coagulate even when excess HCl is added.

Rise of temperature also usually favours coagulation of colloidal solutions. The adsorption of ions, giving rise to the particle charge, is diminished, and the solvate layers may also be destroyed.

The precipitates formed as the result of coagulation are known as *gels.* The well-known jelly formed by gelatin is an example of a gelatinous form of lyophilic colloid gel. A similar type of gel, formed by silicic acid, will be met in our study of the reactions of anions.

It was pointed out earlier that the formation of colloidal solutions complicates analysis, because colloidal particles pass freely through the pores of the filter so that separation becomes impossible. Colloidal solutions must be coagulated in order to separate substances present in the colloidal state. The precipitant itself, which is always added in slight excess*, acts as a coagulant electrolyte. Moreover, an electrolyte (usually an ammonium salt) is also added for the same purpose, and the solution may also be boiled.

The solution must be free from protective colloids for coagulation to occur. Therefore organic substances must be removed before analysis; the unknown substance is usually boiled with a mixture of concentrated HNO_3 and H_2SO_4 for this purpose. This treatment oxidizes organic substances.

Colloidal solutions may also form when precipitates are washed. This is because the coagulant electrolyte added during precipitation is gradually washed out of the precipitate. The precipitated particles therefore acquire charges again and form a colloidal solution (*peptization* effect) which passes readily through the filter. To avoid this undesirable effect, some precipitates have to be washed with a dilute electrolyte solution (usually an ammonium salt) rather than with pure water. The ions of this electrolyte are adsorbed by the precipitate and gradually replace the ions removed by washing, thereby preventing peptization of the precipitate.

42. Coprecipitation

When a precipitate forms, it adsorbs both its own and various extraneous ions on its surface. This adsorption is especially extensive if it occurs on colloidal particles, which have a very large relative surface. The analyst must take adsorption into account, especially during detection of small amounts ("traces") of various impurities.

During separation reactions these small amounts of impurities are often adsorbed completely by the precipitate and cannot be detected in the solution.

The precipitation conditions largely determine which extraneous ions are adsorbed by the precipitate in any particular instance.

* A large excess of precipitant is harmful, because it may lead to reversal of the particle charges with consequent formation of a colloidal solution.

It is found experimentally that ions which are constituents of the colloidal particles are usually adsorbed first, and the particles then acquire the corresponding charge. As they coagulate, these electrically charged particles take extraneous ions of opposite charges with them into the precipitate. For example, when ferric hydroxide is precipitated in ammonia solution the $Fe(OH)_3$ particles adsorb OH^- ions, become negatively charged, and therefore take various cations such as Mg^{++}, Ca^{++}, and especially Co^{++}, Mn^{++}, Ni^{++}, etc., with them into the precipitate when they coagulate; this must be taken into consideration during analysis of Group III cations.

On the other hand, if ferric hydroxide is precipitated in slightly acid solution the $Fe(OH)_3$ particles adsorb Fe^{+++} ions and become positively charged. The precipitate therefore adsorbs various anions (Cl^-, SO_4^{--}, etc.) from the solution. This effect, when extraneous substances which are not themselves precipitated by a given precipitant under the particular conditions are included in the precipitate, is known as *coprecipitation.*

Coprecipitation may also occur in the cracks and microcapillaries which are present in every real crystal (internal adsorption), as well as the result of adsorption of extraneous substances on the surfaces of the precipitated particles. The mechanism of internal adsorption is easily understood: ions adsorbed on the surfaces of the growing crystals of the precipitate, if they do not leave these surfaces in time, are "cut off" from the solution owing to deposition of fresh layers of substance.

A frequent cause of coprecipitation is the precipitation of *mixed crystals*, i.e., crystals formed of two or more substances which crystallize in the same crystalline form. Substances capable of forming mixed crystals are said to be *isomorphous.* This type of coprecipitation is therefore known as *isomorphous coprecipitation*, in distinction from *adsorptional coprecipitation.*

Finally, coprecipitation may sometimes be caused by the formation of true chemical compounds between the precipitate and the coprecipitated impurity. For example, the coprecipitation of Zn^{++} with manganese when the latter is precipitated in the form of the acid* H_2MnO_3 is due to the formation of the insoluble zinc salt of this acid, $ZnMnO_3$, etc. However, this type of coprecipitation is relatively rare. Adsorptional or isomorphous coprecipitation is much more common.

Thus, two cases are distinguished in coprecipitation:

(a) the coprecipitated impurity is on the surface of the precipitated particles (surface adsorption);

---

* Its formula is often written as $MnO(OH)_2$.

(b) the coprecipitated impurity is *occluded* within the particles (internal adsorption, formation of mixed crystals or chemical compounds).

In the former case the adsorbed ions are in dynamic equilibrium with the corresponding ions in solution ("adsorption equilibrium"). When the precipitate is washed, this equilibrium is continuously disturbed and the adsorbed ions gradually pass from the surface of the precipitate into the solution. This means that *impurities adsorbed on the surface can be removed from the precipitate by washing, but occluded impurities cannot be washed out.* The whole precipitate must be dissolved to bring occluded impurities into solution.

If any particular ions are coprecipitated to a considerable extent in separation reactions, they should preferably be detected by fractional methods before separation if possible. Sometimes coprecipitation can be decreased considerably by replacement of some ions by others. For example, if we have to precipitate Ba^{++} by the action of SO_4^{--} ions in the presence of Fe^{+++} ions which are very extensively coprecipitated with $BaSO_4$, it is preferable to reduce them first to Fe^{++} ions, which are coprecipitated much less.

Reprecipitation is a very important measure against coprecipitation, and is frequently used (especially in quantitative analysis). It is illustrated by the following example. If Ca^{++} is precipitated as CaC_2O_4 in the presence of Mg^{++}, a small amount of MgC_2O_4 is coprecipitated. To remove the latter, the precipitate is filtered off, washed slightly and dissolved in HCl. The resultant solution contains all the Ca^{++} present in the original solution and a small portion of the Mg^{++} contained initially in it. If the acid is now neutralized and CaC_2O_4 is reprecipitated, the Mg^{++} concentration during the second precipitation is very much lower than during the first. Therefore the CaC_2O_4 precipitate formed is almost free of MgC_2O_4.

In addition to coprecipitation, the analyst also meets the *delayed precipitation* effect. This is the gradual precipitation of an impurity on standing. For example, in the separation of Group IV from Group III by the action of hydrogen sulphide in acid solution the precipitate initially formed is free from zinc sulphide. However, if the precipitate is filtered off some time after the precipitation it is found to be contaminated with ZnS owing to delayed precipitation of the latter on standing.

The cause of delayed precipitation of zinc sulphide is adsorption of S^{--} ions from solution by particles of Group IV sulphides, so that the suphide ion concentration at the particle surfaces is higher than in solution. Therefore zinc sulphide is precipitated more easily on the surface of other sulphides than in their absence.

We have seen that coprecipitation and delayed precipitation are serious obstacles to many analytical separations. However, copre-

cipitation may also have a favourable effect. It may be used for concentrating certain ions present in solution as traces; this is often utilized in analysis.

For example, if a solution contains traces of Cu^{++} ions, they are not precipitated by H_2S. However, if a small amount of a mercuric salt is added to the solution the HgS precipitate formed by the action of hydrogen sulphide traps the Cu^{++} ions. When the resultant HgS + + CuS precipitate is heated strongly, the mercury is removed (because the HgO formed decomposes into Hg and O_2, which volatilize) and CuS is converted into CuO. The copper oxide is dissolved in a few drops of HCl, and Cu^{++} is easily detected in the solution.

This operation is known as *precipitation with a collector*. In the above example the collector (or carrier) is HgS, which concentrates the Cu^{++} ions so that very small amounts of copper can be detected. Precipitation with collectors is widely used in qualitative and quantitative analysis for detection and determination of traces of various impurities; this is extremely important in many branches of industry and science. The collectors in use at present are fairly numerous; they include manganese dioxide, calomel (Hg_2Cl_2) and certain other salts, sulphur, etc.

QUESTIONS AND PROBLEMS

1. What are the effects of $(NH_4)_2S$ and H_2S on the cations of Groups III and IV? Explain the difference between their behaviour with these reagents.
2. Why is the solution acidified with HCl in the separation of Groups III and IV?
3. Find by calculation whether CdS is precipitated when H_2S is passed through 0.001 *M* $CdCl_2$ solution acidified with HCl to 0.5 *N* concentration.

Answer. It is precipitated.

4. Find the H^+ ion concentrations required to prevent precipitation of the corresponding sulphides when hydrogen sulphide is passed through 0.1 *M* solutions of (a) $FeSO_4$; (b) $ZnSO_4$.

Answer. (a) 0.0014 g-ion/litre; (b) 0.24 g-ion/litre (or higher).

5. The following solutions are saturated with hydrogen sulphide at room temperature: (a) 0.1 *M* $CuSO_4$; (b) 0.1 *M* $CuSO_4$ also containing HCl at 1 *N* concentration. Taking the H_2S concentration in a saturated solution as 0.1 *M*, calculate the concentration of Cu^{++} ions remaining unprecipitated in both cases.

Answer. (a) 5×10^{-23} g-ion/litre; (b) 1.8×10^{-21} g-ion/litre.

6. Hydrogen sulphide is passed through 1 *M* zinc chloride solution, the H^+ ion concentration being maintained at 0.01 g-ion/litre during the precipitation. Calculate the percentage of the total amount of zinc which can be precipitated as ZnS under these conditions.

Answer. 99.98%.

7. At 20° (a) pure water, and (b) 0.1 *N* HCl solution are saturated with carbon dioxide. Taking the concentration of a saturated solution of CO_2 at this temperature as 3.8×10^{-2} *M*, find the CO_3^{--} ion concentrations in both cases. What is the effect of the presence of HCl on the CO_3^{--} ion concentration in this case?

Answer. (a) 5.6×10^{-11} g-ion/litre; (b) 9.2×10^{-17} g-ion/litre; the effect is to lower the concentration in the ratio of 600,000:1.

8. Find by calculation whether $CaCO_3$ ($SP = 4.8 \times 10^{-9}$) and $PbCO_3$ ($SP = 1.5 \times 10^{-13}$) are precipitated when CO_2 gas is passed through 0.2 *N* solutions of the acetates of these metals (see preceding problem).

Answer. $CaCO_3$ is not precipitated; $PbCO_3$ is partially precipitated.

9. What factors influence the solubility of sparingly soluble compounds in acids, ammonium salts and similar reagents?

10. Explain why (a) zinc sulphide dissolves in H_2SO_4 but not in CH_3COOH; (b) in contrast to ZnS, the sulphides of manganese and ferrous iron are soluble in both these acids; (c) bismuth sulphide is insoluble not only in acetic but also in dilute sulphuric and hydrochloric acids; (d) bismuth sulphide, which is insoluble in the above-mentioned acids, dissolves on heating in HNO_3; (e) HgS is insoluble in nitric acid.

11. Explain why (a) CH_3COOH dissolves $SrCrO_4$ but not $BaCrO_4$; (b) the phosphates of aluminium and ferric iron are insoluble in CH_3COOH while most other phosphates which are insoluble in water are dissolved by acetic acid; (c) ferrous hydroxide is soluble both in acids and in ammonium salts while ferric hydroxide dissolves in acids but not in ammonium salts.

12. What are disperse systems? List the classes of disperse systems which you know, indicating the sizes of their dispersed particles.

13. List the properties which distinguish colloidal solutions from suspensions and emulsions on the one hand, and from true solutions on the other.

14. How can colloidal particles be separated from molecules or ions of dissolved substances?

15. Explain why the dispersed particles in colloidal solutions do not join to form larger aggregates. What would happen if they did?

16. Explain how the charges in colloidal particles originate.

17. What is the difference between lyophobic and lyophilic colloids?

18. What is meant by coagulation of colloidal solutions? What causes coagulation of lyophobic and lyophilic colloids?

19. How may the formation of colloidal solutions during precipitation be prevented?

20. What is peptization? How is the peptization of precipitates prevented during washing?

21. What is coprecipitation and why does it occur?

22. Ferric hydroxide is precipitated by the action of NH_4OH on a solution containing Al^{+++} ions in addition to Fe^{+++} ions. Can the precipitation of aluminium ions in the form of $Al(OH)_3$ be described as coprecipitation?

23. What is coprecipitation with a collector? Give an example.

24. What is delayed precipitation?

43. Hydrolysis of Salts

The hydrolysis of salts plays an important part in analysis. For example, the pH of many salt solutions is determined by their hydrolysis. If such salts are used as precipitants, the excess added determines to a considerable extent the pH of the solution and therefore the completeness of precipitation. We have already met such cases in the discussion of the precipitation of Group II and III cations by their group reagents (Sections 33 and 39). It also happens quite often that, because of hydrolysis of the reagents, hydroxides [$Al(OH)_3$, $Cr(OH)_3$, etc.] are precipitated instead of the corresponding sparingly

soluble salts [such as Al_2S_3, $Cr_2(CO_3)_3$, etc.]. All this shows that serious attention must be devoted to the hydrolysis process in studying analytical chemistry.

The interaction of ions of a dissolved salt with H^+ *and* OH^- *ions of water is known as hydrolysis.* The following three cases of hydrolysis are distinguished.

1. Hydrolysis of salts formed from strong bases and weak acids. When a salt such as KCN dissolves in water, the K^+ and CN^- ions meet the OH^- and H^+ ions of water and H^+ ions combine with CN^- ions owing to the formation of the very weak (slightly dissociated) acid HCN ($K = 7.2 \times 10^{-10}$). This may be represented schematically as follows:

$$KCN \longrightarrow K^+ + CN^-$$

$$H_2O \rightleftarrows OH^- + \underset{\uparrow\downarrow}{\overset{+}{H^+}}$$

$$\underset{HCN}{}$$

The OH^- ions of water, however, do not combine with the salt cations because the resulting compound (KOH) is a strong base and as such is dissociated almost completely in dilute solution.

As the H^+ ions are removed the dissociation equilibrium of water is continuously disturbed, so that fresh amounts of H^+ and OH^- ions appear in the solution all the time. However, the H^+ ions combine with CN^- ions while OH^- ions gradually accumulate in the solution. This accumulation must gradually suppress the dissociation of water and lower the resultant concentration of H^+ ions.

On the other hand, the weak acid HCN formed in the reaction is not entirely incapable of dissociation. As it dissociates, it partially returns H^+ and CN^- ions into the solution in amounts which increase with increase of the number of HCN molecules present in the solution.

It is clear that ultimately equilibrium is reached when the amount of H^+ ions combining in unit time to form HCN molecules is equal to the amount appearing in the solution as the result of dissociation. At this state of equilibrium the OH^- ion concentration must evidently be considerably higher than the H^+ ion concentration and the KCN solution must therefore have an alkaline reaction. It is in fact found that the pH of a 1 *N* KCN solution is about 11.6.

The fact that the solution becomes alkaline as the result of hydrolysis of KCN is clearly demonstrated if the equation is written in ionic form. We first write the molecular equation for the reaction, and then the ionic, taking into account that H_2O and HCN are weak electrolytes and should be represented as molecules, while KCN and KOH should be written in ionic form.

Therefore

$$KCN + H_2O \rightleftarrows KOH + HCN$$

$$K^+ + CN^- + H_2O \rightleftarrows K^+ + OH^- + HCN$$

and finally

$$CN^- + H_2O \rightleftarrows OH^- + HCN$$

The equation shows that in this instance hydrolysis is accompanied by an increase of the amount of OH^- ions in solution.

Like KCN, a solution of CH_3COONa also has an alkaline reaction, as is evident from the equation for the hydrolysis of this salt:

$$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-$$

Although this case is very similar to the preceding one, there is a significant difference between the two, because the dissociation constant of CH_3COOH ($K = 1.86 \times 10^{-5}$) is much larger than that of HCN ($K = 7.2 \times 10^{-10}$). Because of this, the removal of H^+ ions cannot go as far as in the case of KCN, and therefore less of the salt is converted at equilibrium into the corresponding base and acid, i.e., the *degree of hydrolysis** of the salt is less. Because of the lower degree of hydrolysis of CH_3COONa, a normal solution of this salt is less alkaline (pH = 9.4) than a KCN solution of equal concentration (pH = 11.6).

2. Hydrolysis of salts formed from weak bases and strong acids. In aqueous solutions of such salts OH^- ions of water are removed while H^+ ions accumulate in solution; for example:

$$NH_4Cl + H_2O \rightleftarrows NH_4OH + HCl$$

or

$$NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+$$

It follows that a solution of NH_4Cl should have an acid reaction because of hydrolysis. In fact, the pH of a 1 *N* NH_4Cl solution is 4.6.

We shall meet this type of hydrolysis in our study of Group III cations, because the hydroxides of this group are very weak bases. Therefore *solutions of salts of Group III cations and strong acids have an acid reaction owing to hydrolysis.*

3. Hydrolysis of salts formed from weak bases and weak acids. In this case both the H^+ and OH^- ions of water are removed, for

---

* The method for calculating the degree of hydrolysis, based on the law of mass action, is given in Sec. 44.

example:

$$\begin{array}{ccc} CH_3COONH_4 & \longrightarrow & NH_4^+ + CH_3COO^- \\ & & + \quad + \\ H_2O & \rightleftarrows & OH^- + H^+ \\ & & \uparrow\downarrow \quad \uparrow\downarrow \\ & & NH_4OH \quad CH_3COOH \end{array}$$

As the dissociation constants of NH_4OH (1.79×10^{-5}) and CH_3COOH (1.86×10^{-5}) are almost the same, H^+ and OH^- ions are removed to the same extent and therefore the solution remains practically neutral (pH $\approx$ 7). However, it is easy to show that hydrolysis does occur, and to a considerable extent (because two processes at once disturb the dissociation equilibrium of water). One need only smell a solution of CH_3COONH_4; it smells of acetic acid and of ammonia simultaneously.

It is obvious that solutions of such salts will have a neutral reaction only if the base and acid formed by hydrolysis have similar dissociation constants, i.e., if they are of practically equal strengths. Therefore solutions of salts like $(NH_4)_2S$ or $(NH_4)_2CO_3$, formed from bases which are stronger than the corresponding acids, are weakly alkaline in solution.

When salts of strong acids and strong bases, such as NaCl, KNO_3, etc., are dissolved in water, neither H^+ nor OH^- ions of water are removed, because this would result in the formation of strong (i.e., totally dissociated) acids and bases. *Therefore such salts do not undergo hydrolysis and their solutions have the same reaction as pure water* (pH = 7).

It is seen from all the foregoing that *hydrolysis is caused by disturbance of the dissociation equilibrium of water owing to the formation of weakly dissociated compounds. If such compounds cannot be formed, i.e., if a salt is formed from a strong acid and a strong base, hydrolysis does not occur. Conversely, the weaker the acid or base, the greater is the disturbance of the equilibrium between water molecules and its ions, and the greater is the degree of hydrolysis of the salt.* All this is summarized in Table 14.

So far we have considered the hydrolysis of salts of monobasic acids, in which the reactions products are free bases and acids.

The hydrolysis of salts of di- and polybasic acids is complicated by the fact that *in accordance with the stepwise dissociation of these acids the hydrolysis also occurs in stages.* For example, the hydrolysis of Na_2CO_3 can be represented by the equations:

first stage

$$Na_2CO_3 + H_2O \rightleftarrows NaHCO_3 + NaOH$$

or

$$CO_3^{2-} + H_2O \rightleftarrows HCO_3^- + OH^-$$

second stage

$$NaHCO_3 + H_2O \rightleftarrows H_2CO_3 + NaOH$$

or

$$HCO_3^- + H_2O \rightleftarrows H_2CO_3 + OH^-$$

Since HCO_3^- anions ($K_2 = 5.61 \times 10^{-7}$) are dissociated far less than H_2CO_3 molecules ($K_1 = 4.31 \times 10^{-7}$), *the first stage of hydrolysis is far more extensive than the second.* Similarly, the hydrolysis of

Table 14

Hydrolysis of Salts

Salt from		Hydrolysis	Reaction of solution
base	acid		
Strong	Weak	Occurs	Alkaline (pH > 7)
Weak	Strong	Occurs	Acid (pH < 7)
Weak	Weak	Extensive	Near to neutral (pH≈7), dependent on the relative strengths of the acid and base
Strong	Strong	Does not occur	Neutral (pH ≈ 7) *

* The reaction of the solution depends on the pH of the water used.

Na_3PO_4 occurs in three stages, of which the most extensive is the first, corresponding to the equation

$$Na_3PO_4 + H_2O \rightleftarrows Na_2HPO_4 + NaOH$$

It must be clearly understood that the stepwise hydrolysis of a salt (e.g., Na_2CO_3) cannot be represented by the overall equation

$$Na_2CO_3 + 2H_2O \rightleftarrows H_2CO_3 + 2NaOH$$

obtained by addition of the equations for the individual stages. When the equations are added, the common term $NaHCO_3$ cancels out. This would be permissible only if all the $NaHCO_3$ formed at the first stage was converted into H_2CO_3 in accordance with the second-stage equation. In fact only a minute proportion of the $NaHCO_3$ is converted into H_2CO_3, while most of it remains in solution and is the *main* hydrolysis product, and yet the overall equation given above

does not contain it at all. To represent the hydrolysis of Na_2CO_3 by a single equation, it should be written as follows:

$$\begin{array}{l} x\mathrm{Na_2CO_3}+x\mathrm{H_2O}=x\mathrm{NaHCO_3}+x\mathrm{NaOH} \\ y\mathrm{NaHCO_3}+y\mathrm{H_2O}=y\mathrm{H_2CO_3}+y\mathrm{NaOH} \\ \hline x\mathrm{Na_2CO_3}+(x+y)\mathrm{H_2O}=(x-y)\mathrm{NaHCO_3}+y\mathrm{H_2CO_3}+(x+y)\mathrm{NaOH} \end{array}$$

such that $x \gg y$.

It is seen that hydrolysis of salts of di- and polybasic acids leads to the formation of acid salts. Basic salts are formed as the result of hydrolysis of salts of bi- and multivalent metals. For example, we saw on p. 86 that when $MgCl_2$ solution is evaporated one of the Cl^- ions of the salt molecule is replaced by an OH^- ion from water to give the basic salt MgOHCl:

$$\mathrm{MgCl_2}+\mathrm{H_2O} \rightleftarrows \mathrm{MgOHCl}+\mathrm{HCl}$$

Similarly, the hydrolysis of $(CH_3COO)_3Fe$ can be represented by the following equations:
first stage

$$(\mathrm{CH_3COO})_3\mathrm{Fe}+\mathrm{H_2O} \rightleftarrows (\mathrm{CH_3COO})_2\mathrm{OHFe}+\mathrm{CH_3COOH}$$

second stage

$$(\mathrm{CH_3COO})_2\mathrm{OHFe}+\mathrm{H_2O} \rightleftarrows \mathrm{CH_3COO(OH)_2Fe}+\mathrm{CH_3COOH}$$

third stage

$$\mathrm{CH_3COO(OH)_2Fe}+\mathrm{H_2O} \rightleftarrows \mathrm{Fe(OH)_3}+\mathrm{CH_3COOH}$$

As was pointed out in Sec. 31, in the light of the protolytic theory of acids and bases hydrolysis is a typical protolytic reaction. In the case of CH_3COONa we have

$$\begin{array}{llll} \mathrm{CH_3COO^-}+\mathrm{H_2O} \rightleftarrows & \mathrm{CH_3COOH}+\mathrm{OH^-} \\ \mathrm{Base_1} \quad \mathrm{Acid_2} & \mathrm{Acid_1} \quad \mathrm{Base_2} \end{array}$$

Similarly, for NH_4Cl we can write

$$\begin{array}{llll} \mathrm{NH_4^+}+\mathrm{H_2O} \rightleftarrows & \mathrm{NH_3}+\mathrm{H_3O^+} \\ \mathrm{Acid_1} \quad \mathrm{Base_2} & \mathrm{Base_1} \quad \mathrm{Acid_2} \end{array}$$

The following reactions occur in the hydrolysis of aluminium salts:

$$\mathrm{Al(OH_2)_6^{+++}}+\mathrm{H_2O} \rightleftarrows \mathrm{Al(OH_2)_5OH^{++}}+\mathrm{H_3O^+} \text{ (stage I)}$$

$$\mathrm{Al(OH_2)_5OH^{++}}+\mathrm{H_2O} \rightleftarrows \mathrm{Al(OH_2)_4(OH)_2^+}+\mathrm{H_3O^+} \text{ (stage II)}$$

$$\begin{array}{llll} \mathrm{Al(OH_2)_4(OH)_2^+}+\mathrm{H_2O} \rightleftarrows & \mathrm{Al(OH_2)_3(OH)_3}+\mathrm{H_3O^+} & \text{(stage III)} \\ \mathrm{Acid_1} \quad \mathrm{Base_2} & \mathrm{Base_1} \quad \mathrm{Acid_2} \end{array}$$

It follows from all the foregoing that hydrolysis is a reversible process leading to a state of equilibrium. In most cases at equilibrium

only a small proportion of the salt is changed into other substances. However, if a hydrolysis product is formed in such large amounts that it can be precipitated or volatilized in the form of gas the hydrolysis becomes irreversible and leads to practically complete decomposition of the salt by water. An example of this is the hydrolysis of Al_2S_3:

$$Al_2S_3 + 6H_2O \longrightarrow \downarrow 2Al(OH)_3 + 3H_2S \uparrow$$

It is evident that such salts can exist only in the absence of water.

In many analytical reactions the hydrolysis of the salts used as reagents must be taken into account, as quite often it is the hydrolysis products and not the salt ions which are involved in the reaction. This is illustrated by the following example.

Most of the Group III cations are precipitated by the group reagent $(NH_4)_2S$ as the sulphides: FeS, MnS, ZnS, etc. However, in the case of Al^{+++} and Cr^{+++} the hydroxides $Al(OH)_3$ and $Cr(OH)_3$ and not the sulphides are formed. The reason is easily seen if it is remembered that as the result of hydrolysis $(NH_4)_2S$ contains considerable amounts of HS^- and OH^- anions in addition to S^{--}. It was explained in Sec. 27 that if a solution contains several different kinds of ions which can be precipitated by an ion of opposite charge, the compound whose solubility product is reached first is the one to be precipitated. In the case of Fe^{++}, Mn^{++}, Zn^{++}, etc., the solubility products of the sulphides are reached first. Therefore the sulphides and not the hydroxides of these metals are precipitated by $(NH_4)_2S$. On the other hand, in the case of Al^{+++} and Cr^{+++} the solubility products of the hydroxides are evidently reached first*.

Accordingly, the reaction between $(NH_4)_2S$ and $Al_2(SO_4)_3$ can be represented by the following equations:

$$3(NH_4)_2S + 3H_2O \rightleftarrows 3NH_4HS + 3NH_4OH$$

$$3NH_4HS + 3H_2O \rightleftarrows 3H_2S + 3NH_4OH$$

$$Al_2(SO_4)_3 + 6NH_4OH = \downarrow 2Al(OH)_3 + 3(NH_4)_2SO_4$$

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = \downarrow 2Al(OH)_3 + 3(NH_4)_2SO_4 + 3H_2S \uparrow$$

* This explanation, based on the general laws of precipitation, can be confirmed by calculation from the solubility products (see Sec. 27) only in the case of the ions precipitated as sulphides. In the case of Al^{+++} and Cr^{+++}, the sulphides of which are completely decomposed by water (see above) and can be obtained only in the absence of water, the solubility products of the sulphides are unknown and the calculation is impossible. It should be noted that in this case the mechanism of the reaction with $(NH_4)_2S$ can be interpreted in another way (see p. 207).

Note that the same equation would be obtained if the hydrolysis of $(NH_4)_2S$ is represented by the overall equation

$$(NH_4)_2S + 2H_2O = H_2S + 2NH_4OH$$

However, it must be clearly understood that *such a simplification is permissible only if the individual stages of hydrolysis go practically to completion.* This occurs, for example, when one of the hydrolysis products is involved in a further reaction.

In the present instance $(NH_4)_2S$ is hydrolyzed predominantly according to the equation

$$(NH_4)_2S + H_2O \rightleftarrows NH_4HS + NH_4OH$$

and the main hydrolysis product is an acid salt; there is no indication of the formation of this salt in the overall equation given above for the hydrolysis of ammonium sulphide. Despite this, it can be used for deriving the equation for the reaction with an aluminium salt, because as NH_4OH becomes consumed for precipitation of Al^{+++} the hydrolysis equilibrium of NH_4HS

$$NH_4HS + H_2O \rightleftarrows NH_4OH + H_2S$$

is disturbed and eventually all of the acid salt is converted into H_2S. This is why the overall equation for the hydrolysis of $(NH_4)_2S$ can be used in the present instance.

There are other instances when we have to take into account the shift of hydrolysis equilibrium due to consumption of one of the hydrolysis products in a reaction. For example, if an alkali is added slowly to $AlCl_3$ solution, as the hydrochloric acid formed by hydrolysis is neutralized fresh amounts of this acid and of aluminium hydroxide are formed and eventually the latter is precipitated:

$$AlCl_3 + 3H_2O \rightleftarrows Al(OH)_3 + 3HCl$$

$$3HCl + 3NaOH = 3NaCl + 3H_2O$$

However, it is clear that so long as the solution contains $AlCl_3$ it will remain acidic owing to hydrolysis. Therefore *it is impossible to eliminate by neutralization the acidity of solutions of salts of Group III cations which results from hydrolysis.* If we nevertheless sometimes speak of the neutralization of such solutions, we refer to the acids added to the solutions and not to the acids formed by hydrolysis. The added acid can be neutralized as follows. An alkali is added drop by drop to the solution until a turbidity due to hydroxide appears and persists when the liquid is stirred; this turbidity is dissolved in one or two drops of acid and the neutralization is then regarded as complete. Although this solution is still acid to litmus, the acidity is due only to the acid formed as the result of hydrolysis.

The formation of aluminium and chromium hydroxides when ammonium sulphide is added to solutions of aluminium and chromium salts can also be attributed to disturbance of the hydrolysis equilibrium (see the explanation given on p. 205). For example,

$$2AlCl_3 + 6H_2O \rightleftarrows 2Al(OH)_3 + 6HCl$$

$$6HCl + 3(NH_4)_2S = 6NH_4Cl + 3H_2S$$

$$2AlCl_3 + 3(NH_4)_2S + 6H_2O = \downarrow 2Al(OH)_3 + 6NH_4Cl + 3H_2S \uparrow$$

It must be remembered that hydrolysis may often interfere with analysis, and must therefore be suppressed.

While hydrolysis is intensified by removal of one of the hydrolysis products, it is suppressed by the addition of such a product. This fact is widely used in the storage of solutions of easily hydrolyzed salts. For example, an aqueous solution of an iron salt such as $Fe_2(SO_4)_3$ soon forms a precipitate of basic salt as the result of hydrolysis. If the solution is acidified, so that H^+ ions, one of the hydrolysis products, are introduced, the reaction opposing hydrolysis predominates and the solution is more stable on keeping.

Similarly, hydrolysis of salts of weak acids (KCN, CH_3COONa, etc.) is suppressed by the introduction of OH^- ions, the hydrolysis product in this case. This raises the concentration of the salt anions (CN^-, CH_3COO^-) in solution.

As was stated earlier, the group reagent for Group III, $(NH_4)_2S$, is hydrolyzed mainly at the first stage:

$$(NH_4)_2S + H_2O \rightleftarrows NH_4OH + NH_4HS$$

or

$$NH_4^+ + S^{--} + H_2O \rightleftarrows NH_4OH + HS^-$$

Since both the hydrolysis products, NH_4OH and HS^- ions, are only slightly dissociated, the degree of hydrolysis of $(NH_4)_2S$ is very high; calculation (see Sec. 44) shows that it is about 99.9%. It follows that in this case the S^{--} ion concentration is very much lowered by hydrolysis. However, it is known that the lower the concentration of the precipitant ion the less complete the precipitation (Sec. 26). Therefore the degree of hydrolysis of $(NH_4)_2S$ must be lowered in order to achieve adequate precipitation of Group III cations. This is done by addition of NH_4OH to the $(NH_4)_2S$ solution, which shifts the hydrolysis equilibrium to the left and raises the S^{--} ion concentration. It will be remembered that hydrolysis of ammonium carbonate is suppressed in a similar way in precipitation of Group II cations.

It is therefore clear that *the hydrolysis of salts may be suppressed by appropriate regulation of the solution* pH.

Moreover, the temperature and concentration of the salt solution have a strong influence on hydrolysis equilibrium. This is discussed more fully in the next section.

Thus, *the degree of hydrolysis of a salt is decreased by the addition of one of the hydrolysis products. Conversely, hydrolysis is intensified by removal of such a product.*

44. Degree of Hydrolysis and the pH of Salt Solutions

The degree of hydrolysis is the fraction hydrolyzed of the total amount of salt present, i.e., the fraction converted by the action of H_2O into the corresponding acid and base (or into acid or basic salts). The degree of hydrolysis is not difficult to calculate from the equation for the dissociation constant of the corresponding weak acid (or base) and the ionic product of water. The following example demonstrates the calculation in the case of KCN, the hydrolysis of which can be represented by the following ionic equation:

$$CN^- + H_2O \rightleftarrows HCN + OH^-$$

We first write the equation for the equilibrium constant of this reaction

$$\frac{[OH^-]\cdot[HCN]}{[CN^-]\cdot[H_2O]} = K$$

Since water, which is the solvent, is present in enormous excess in dilute solutions its concentration remains practically constant whatever the shift of the hydrolysis equilibrium may be. Therefore $[H_2O]$ may be taken as constant and transferred to the right-hand side of the equation:

$$\frac{[OH^-]\cdot[HCN]}{[CN^-]} = K\cdot[H_2O] = K_h \qquad (1)$$

The product of two constants, $K\cdot[H_2O]$, is itself constant; it is known as the *hydrolysis constant*, denoted by K_h. The numerical value of K_h is easily found from K_{H_2O} and K_{HCN}. The equation for the ionic product of water

$$[H^+]\cdot[OH^-] = K_{H_2O}$$

gives

$$[OH^-] = \frac{K_{H_2O}}{[H^+]}$$

Substituting this value of $[OH^-]$ into Eq. (1), we have

$$\frac{K_{H_2O}\cdot[HCN]}{[H^+]\cdot[CN^-]} = K_h$$

or

$$\frac{K_{H_2O}}{K_{HCN}} = K_h$$

Therefore*

$$\frac{[OH^-]\cdot[HCN]}{[CN^-]} = \frac{K_{H_2O}}{K_{acid}} \tag{2}$$

The required degree of hydrolysis can be found from Eq. (2). Let the concentration of the salt be c mole/litre; if the degree of hydrolysis is h, ch moles of the salt must be hydrolyzed to give ch moles of HCN and ch g-ions of OH^-. We can therefore write

$$\frac{c^2h^2}{c-ch} = \frac{K_{H_2O}}{K_{acid}}$$

and hence

$$\frac{ch^2}{1-h} = \frac{K_{H_2O}}{K_{acid}} \tag{2a}$$

Since h is usually very small compared with unity, we can assume that

$$ch^2 \approx \frac{K_{H_2O}}{K_{acid}}$$

and

$$h \approx \sqrt{\frac{K_{H_2O}}{c\cdot K_{acid}}} \tag{3}$$

Equation (3) shows that *the degree of hydrolysis increases with*:
(a) *increase of* K_{H_2O}, *i.e., rise of temperature*;
(b) *decrease of* K_{acid}, *i.e., with increasing weakness of the acid the salt of which is hydrolyzed*;
(c) *decrease of* c, *i.e., with increasing dilution.*

For example, if we substitute numerical values into Eq. (3), for 1 M KCN solution ($K_{HCN} = 7.2 \times 10^{-10}$) we have $h \approx 1.2 \times 10^{-2}$ or 1.2%. The degree of hydrolysis of 1 M CH_3COONa solution ($K_{CH_3COOH} = 1.86 \times 10^{-5}$) is only about 0.007%.

It is easy to derive in a similar manner a formula for calculating the degree of hydrolysis of a salt of a strong acid and a weak base. For NH_4Cl we have

$$K_h = \frac{[H^+]\cdot[NH_4OH]}{[NH_4^+]} = \frac{K_{H_2O}}{K_{base}}$$

and hence

$$h \approx \sqrt{\frac{K_{H_2O}}{c\cdot K_{base}}} \tag{4}$$

* K_{acid} is the dissociation constant of the weak acid formed by hydrolysis; K_{HCN} in this example.

Thus, all the above relationships are applicable here too, except that the denominator contains K_{base} instead of K_{acid}.

The degree of hydrolysis of 1 *M* NH_4Cl solution is found to be about 0.007%.

It must be remembered that Equations (3) and (4) are applicable only if the degree of hydrolysis is low. If it is high, as in the case of Na_2S or Na_3PO_4, Eq. (2a) must be used. It is solved as complete quadratic equation.

Let us now consider the calculation of the degree of hydrolysis of salts like CH_3COONH_4, formed from a weak base and a weak acid.

The ionic equation for the hydrolysis of ammonium acetate

$$NH_4^+ + CH_3COO^- + H_2O \rightleftarrows NH_4OH + CH_3COOH$$

gives

$$K_h = \frac{[NH_4OH] \cdot [CH_3COOH]}{[NH_4^+] \cdot [CH_3COO^-]} \tag{5}$$

and we also have from the equations for the dissociation constants of CH_3COOH and NH_4OH:

$$[CH_3COOH] = \frac{[H^+] \cdot [CH_3COO^-]}{K_{acid}} \text{ and } [NH_4OH] = \frac{[NH_4^+] \cdot [OH^-]}{K_{base}}$$

Substituting these into Eq. (5) and replacing $[H^+] \cdot [OH^-]$ by K_{H_2O}, we have

$$K_h = \frac{K_{H_2O}}{K_{acid} \cdot K_{base}} \tag{6}$$

As before, we denote the total concentration of the salt by c and the degree of hydrolysis by h. Then the number of moles of salt hydrolyzed is ch. Since each molecule of the salt gives one molecule each of CH_3COOH and NH_4OH on hydrolysis, we have

$$[CH_3COOH] = [NH_4OH] = ch \text{ moles/litre}$$

The concentration of the unhydrolyzed salt is $c - ch = c(1 - h)$ moles/litre. Assuming the salt to be completely dissociated, we can write

$$[CH_3COO^-] = [NH_4^+] = c(1-h) \text{ g-ions/litre}$$

Putting the values found for the concentrations into Eq. (5) and taking Eq. (6) into account, we have

$$\frac{ch \cdot ch}{c(1-h) \cdot c(1-h)} = \frac{K_{H_2O}}{K_{base} \cdot K_{acid}}$$

or

$$\frac{h^2}{(1-h)^2} = \frac{K_{H_2O}}{K_{base} \cdot K_{acid}}$$

Taking square roots of both sides of this equation, we have

$$\frac{h}{1-h}=\sqrt{\frac{K_{H_2O}}{K_{acid}\cdot K_{base}}} \tag{7}$$

In this case the denominator in the expression for the hydrolysis constant [see Eq. (6)] is the product of two small quantities; therefore these constants are fairly large. This means that *in this case the hydrolysis is particularly extensive*, as may be readily confirmed by calculation with the aid of Eq. (7). As an example, let us calculate the degree of first-stage hydrolysis of the group reagent for Group III, ammonium sulphide. In this case the hydrolysis reaction is

$$(NH_4)_2S+H_2O \rightleftarrows NH_4HS+NH_4OH$$

or, in ionic form

$$NH_4^+ + S^{--} + H_2O \rightleftarrows HS^- + NH_4OH$$

In Eq. (7) K_{base} is $K_{NH_4OH}=1.79\times10^{-5}$, and K_{acid} is the dissociation constant of the HS^- ion to give H^+ and S^{--} ions, i.e., the second dissociation constant of H_2S ($K_2=1.2\times10^{-15}$). Therefore

$$\frac{h}{1-h}=\sqrt{\frac{1\times10^{-14}}{1.79\times10^{-5}\times1.2\times10^{-15}}}=682.2$$

Hence

$$h=\frac{682.2}{683.2}=0.9986$$

Therefore *ammonium sulphide is hydrolyzed almost completely* (99.86%) *in aqueous solution*; that is, it is converted into the corresponding acid salt.*

We now calculate the second-stage degree of hydrolysis of $(NH_4)_2S$:

$$NH_4HS+H_2O \rightleftarrows H_2S+NH_4OH$$

This depends on the first dissociation constant of H_2S, which is $K_1=5.7\times10^{-8}$. In this case

$$\frac{h}{1-h}=\sqrt{\frac{1\times10^{-14}}{1.79\times10^{-5}\times5.7\times10^{-8}}}=0.099$$

and $h\approx0.09$, i.e., 9% of the acid molecules undergo hydrolysis.

It should be noted that Eq. (7) does not contain c. Thus, in contrast to the cases considered earlier, the degree of hydrolysis of a salt formed from a weak acid and a weak base does not depend on the concentration.

* As was pointed out in Sec. 43, in order to avoid a large decrease in the S^{--} ion concentration the hydrolysis of ammonium sulphide is suppressed by addition of ammonia.

Calculation of the pH of hydrolyzed salt solutions. The expressions for K_h can be used for such calculations. For example, the following expression has been derived for the hydrolysis of KCN:

$$\frac{[OH^-]\cdot[HCN]}{[CN^-]}=\frac{K_{H_2O}}{K_{acid}}$$

But the equation for the hydrolysis reaction

$$CN^- + H_2O \rightleftarrows HCN + OH^-$$

shows that equal amounts of OH^- ions and HCN molecules are formed. Therefore $[OH^-] = [HCN]$. On the other hand, neglecting the relatively small amount of CN^- ions undergoing hydrolysis we can assume that $[CN^-] = c_{salt}$. We can then write

$$\frac{[OH^-]^2}{c_{salt}}=\frac{K_{H_2O}}{K_{acid}}$$

and hence

$$[OH^-]=\sqrt{\frac{K_{H_2O}\cdot c_{salt}}{K_{acid}}}$$

and

$$pOH = 7 - 1/2pK_{acid} - 1/2 \log c_{salt}$$

This gives

$$pH = 14 - pOH = 7 + 1/2pK_{acid} + 1/2 \log c_{salt} \qquad (8)$$

Analogously, the following formula is easily derived for salts of strong acids and weak bases:

$$pH = 7 - 1/2\ pK_{base} - \log c_{salt} \qquad (9)$$

The following equation has been derived for the hydrolysis of a salt of a weak monobasic acid and a weak base (CH_3COONH_4):

$$K_h=\frac{[CH_3COOH]\cdot[NH_4OH]}{[CH_3COO^-]\cdot[NH_4^+]}=\frac{K_{H_2O}}{K_{acid}\cdot K_{base}}$$

$$[CH_3COOH]=[NH_4OH] \text{ and } [CH_3COO^-]=[NH_4^+]=c_{salt}$$

From this we have

$$\frac{[CH_3COOH]^2}{c_{salt}^2}=\frac{K_{H_2O}}{K_{acid}\cdot K_{base}}$$

But, since

$$[CH_3COOH]=\frac{[H^+]\cdot[CH_3COO^-]}{K_{acid}}=\frac{[H^+]\cdot c_{salt}}{K_{acid}}$$

the above equation can be written as follows:

$$\frac{[H^+]^2 \cdot c_{salt}^2}{K_{acid}^2 \cdot c_{salt}^2} = \frac{K_{H_2O}}{K_{acid} \cdot K_{base}}$$

Hence

$$[H^+] = \sqrt{\frac{K_{H_2O} \cdot K_{acid}}{K_{base}}}$$

Finally, taking logarithms of the last expression and reversing the signs, we have

$$pH = 7 + 1/2pK_{acid} - 1/2pK_{base} \qquad (10)$$

Equation (10) is used for calculating the pH of solutions of salts of weak acids and weak bases.

Let us calculate the pH of CH_3COONH_4 solution. In this case $pK_{acid} = -\log 1.86 \times 10^{-5} = 4.73$ and $pK_{base} = -\log 1.79 \times 10^{-5} = 4.75$. Therefore $pH = 7 + 4.73 - 4.75 = 6.98$.

It should be noted that Equations (7) and (10), derived for calculating the degree of hydrolysis and pH of solutions of salts formed by weak acids and weak bases, are applicable only when the charges of the salt anions and cations are of equal magnitude, as in the case of CH_3COONH_4, NH_4CN, etc. Only then can we assume that $c_{cation} = c_{anion} = c - ch = c(1 - h)$; this assumption is obviously inadmissible for salts such as $(NH_4)_2CO_3$, $(NH_4)_2S$, etc., which yield two cations for each anion on dissociation.

The calculations in such cases are illustrated by the following examples.

Example 1. Calculate the equilibrium concentrations of the ions formed by hydrolysis of 0.1 *M* $(NH_4)_2S$ solution and find the pH of the solution.

Solution. The hydrolysis of $(NH_4)_2S$ corresponds mainly to the equation

$$(NH_4)_2S + H_2O \rightleftarrows NH_4HS + NH_4OH$$

or

$$NH_4^+ + S^{--} + H_2O \rightleftarrows HS^- + NH_4OH \qquad (a)$$

The hydrolysis constant corresponding to this equation is

$$K_h = \frac{[HS^-] \cdot [NH_4OH]}{[S^{--}] \cdot [NH_4^+]} = \frac{K_{H_2O}}{K_{HS^-} \cdot K_{NH_4OH}} =$$

$$= \frac{10^{-14}}{1.2 \times 10^{-15} \times 1.8 \times 10^{-5}} = 4.6 \times 10^5 \qquad (b)$$

The second-stage hydrolysis of ammonium sulphide

$$HS^- + NH_4^+ + H_2O \rightleftarrows H_2S + NH_4OH$$

has the constant

$$K_h = \frac{[H_2S] \cdot [NH_4OH]}{[HS^-] \cdot [NH_4^+]} = \frac{K_{H_2O}}{K_{H_2S} \cdot K_{NH_4OH}} = \frac{10^{-14}}{5.7 \times 10^{-8} \times 1.8 \times 10^{-5}} = 1 \times 10^{-2}$$

It is seen that the first hydrolysis constant is 46 million times as large as the second. Therefore the second stage of hydrolysis may be neglected in solving this problem and the calculation may be made with the aid of Equation (a). Since $(NH_4)_2S$ is a strong electrolyte which dissociates almost completely in solution, 0.1 mole gives 0.1 g-ion of S^{--} and 0.2 g-ion of NH_4^+. The concentration* of S^{--} ions at equilibrium is denoted by x. Since the initial S^{--} ion concentration was 0.1 g-ion/litre, we may conclude that $(0.1-x)$ g-ion of S^{--} per litre of solution was removed as the result of the hydrolysis reaction. But the reaction equation (a) shows that when 1 g-ion of S^{--} is removed 1 g-ion of NH_4^+ is consumed with formation of 1 g-ion of HS^- and 1 mole of NH_4OH. Accordingly, we can express the equilibrium concentrations of all the substances involved in the reaction in terms of x:

$$[S^{--}]=x,\ [NH_4^+]=0.2-(0.1-x)=0.1+x$$
$$[HS^-]=[NH_4OH]=0.1-x$$

Substituting these results into Equation (b) for the hydrolysis constant, we have

$$\frac{(0.1-x)^2}{x\cdot(0.1+x)}=4.6\times10^5$$

The large value of K_h shows that the hydrolysis of $(NH_4)_2S$ is very extensive; therefore x must be very much smaller than 0.1 and can be disregarded. We then have

$$\frac{(0.1)^2}{0.1\cdot x}=4.6\times10^5$$

and hence

$$x=2.2\times10^{-7}$$

Consequently**

$$[S^{--}]=x=2.2\times10^{-7}\text{ g-ion/litre}$$
$$[HS^-]=[NH_4OH]=0.1-x=0.1-2.2\times10^{-7}\approx0.1\text{ g-ion/litre}$$
$$[NH_4^+]=0.1+x=0.1+2.2\times10^{-7}\approx0.1\text{ g-ion/litre}$$

Further, substituting the concentrations of NH_4OH and NH_4^+ into the equation for the dissociation constant of ammonium hydroxide, we have

$$\frac{[NH_4^+]\cdot[OH^-]}{[NH_4OH]}=\frac{0.1\cdot[OH^-]}{0.1}=1.8\times10^{-5}$$

---

* In calculating equilibrium concentrations from the equation of the mass action law, the lowest concentration must be taken as x. It is easy to determine from the equilibrium constant which of the concentrations is the lowest. In the present instance the enormous value $K_h = 4.6 \times 10^5$ shows that the first-stage hydrolysis goes almost to completion. Therefore the equilibrium concentrations of the reaction products, i.e., HS^- ions and NH_4OH molecules, must be high while the concentration of the residual S^{--} ions is low. This last concentration must be taken as x. To confirm the validity of the mathematical rule according to which the lowest of the equilibrium concentrations must be taken as the unknown, attempt to solve the same problem taking the HS^- ion concentration as x.

** The value found for x (2.2×10^{-7}) shows that it was permissible to disregard it in comparison with 0.1.

Therefore

$$[OH^-]=1.8\times10^{-5}\ \text{g-ion/litre};\quad pOH=-\log 1.8\times10^{-5}=4.75$$

and

$$pH=14-4.75=9.25$$

Example 2. Calculate the equilibrium concentrations of the ions formed by hydrolysis of 0.1 *M* $(NH_4)_2CO_3$, and find the pH of the solution.

Solution. The hydrolysis of ammonium carbonate proceeds in stages:

$$NH_4^+ + CO_3^{--} + H_2O \rightleftarrows HCO_3^- + NH_4OH \text{ (first stage of hydrolysis)}$$

$$NH_4^+ + HCO_3^- + H_2O \rightleftarrows H_2CO_3 + NH_4OH \text{ (second stage of hydrolysis)}$$

The first-stage hydrolysis constant is

$$\frac{[HCO_3^-]\cdot[NH_4OH]}{[NH_4^+]\cdot[CO_3^{--}]}=\frac{10^{-14}}{1.8\times10^{-5}\times5.6\times10^{-11}}=10$$

The second-stage constant is

$$\frac{[H_2CO_3]\cdot[NH_4OH]}{[NH_4^+]\cdot[HCO_3^-]}=\frac{10^{-14}}{1.8\times10^{-5}\times4.3\times10^{-7}}=1.3\times10^{-3}$$

Here again the first constant is very much larger than the second, as in the example with $(NH_4)_2S$, and the second hydrolysis stage may be disregarded.

Denoting the CO_3^{--} ion concentration at equilibrium by x, we have

$$[CO_3^{--}]=x;\quad [HCO_3^-]=[NH_4OH]=0.1-x$$
$$[NH_4^+]=0.2-(0.1-x)=0.1+x$$

Therefore

$$\frac{(0.1-x)^2}{(0.1+x)\cdot x}=10$$

In this case x is not negligible in comparison with 0.1. We therefore rearrange the above expression to give the quadratic equation

$$9x^2+1.2x-0.01=0$$

Solving this, we have

$$x=\frac{-0.6+\sqrt{0.36+0.36}}{2\times9}=0.014=1.4\times10^{-2}$$

Therefore

$$[CO_3^{--}]=1.4\times10^{-2}\ \text{g-ion/litre}$$
$$[HCO_3^-]=[NH_4OH]=0.1-0.014=0.086\ \text{g-ion/litre}$$
$$[NH_4^+]=0.1+0.014=0.114\ \text{g-ion/litre}$$

Substituting for $[NH_4OH]$ and $[NH_4^+]$ in the equation

$$pH=14-4.75+\log\frac{[NH_4OH]}{[NH_4^+]}$$

we find

$$pH=9.25-0.12=9.13$$

The results of the calculations in Examples 1 and 2 are very significant. If we compare the equilibrium HS^- ion concentration (Example 1) with the initial S^{--} ion concentration (0.1 g-ion/litre) we find that the S^{--} ions are converted almost completely into HS^- ions as the result of hydrolysis. It follows that *the degree of hydrolysis of ammonium sulphide at the first stage is almost exactly* 100%.

The calculations also showed that the concentrations of NH_4OH and of NH_4^+ ions in 0.1 *M* $(NH_4)_2S$ solution are almost equal to 0.1 *M*. This means that *0.1. M ammonium sulphide solution is really a 0.1 N ammonium buffer mixture; this is confirmed by the* pH *value found, 9.25.*

Table 15

Degree of Hydrolysis and pH of 0.1 *M* Solutions of Certain Salts *

(at 18-25°)

Salt	Weak electrolytes formed by hydrolysis		Degree of hydrolysis %	Solution pH
	formula	dissociation constant		
CH_3COONa	CH_3COOH	1.8×10^{-5}	0.007	8.8
NH_4Cl	NH_4OH	1.8×10^{-5}	0.007	5.2
KCN	HCN	7×10^{-10}	1.2	11.1
NH_4CN	HCN and NH_4OH	see above	46.8	9.2
Na_2SO_3	HSO_3^-	5×10^{-6}	0.014	9.2
$NaHSO_3$	H_2SO_3	1.3×10^{-2}	0.0003	3.6
Na_2CO_3	HCO_3^-	5.6×10^{-11}	4.2	11.6
$NaHCO_3$	H_2CO_3	4.3×10^{-7}	0.05	8.3
$(NH_4)_2CO_3$	HCO_3^- and NH_4OH	see above	85	9.13
CH_3COONH_4	CH_3COOH and NH_4OH	" "	0.6	7.0
Na_3PO_4	HPO_4^{--}	2.2×10^{-13}	48.4	12.8
Na_2HPO_4	$H_2PO_4^-$	6.2×10^{-8}	0.13	9.9
NaH_2PO_4	H_3PO_4	7.5×10^{-3}	0.0004	4.6
Na_2S	HS^-	1.2×10^{-15}	98	13
NaHS	H_2S	5.7×10^{-8}	0.13	11
$(NH_4)_2S$	HS^- and NH_4OH	see above	100	9.25
NH_4HS	H_2S and NH_4OH	" "	9.9	8.3
NaClO	HClO	3×10^{-8}	0.18	10.3

* Some of the dissociation constants are rounded off. The pH of an acid salt is taken as the average of the corresponding pK values of the acid. For example, in the case of $NaHCO_3$ $pH=\frac{1}{2}(pK_1+pK_2)=\frac{1}{2}(6.37+10.25)=8.3$.

In the case of ammonium carbonate (Example 2), since the dissociation constants of carbonic acid are not as low as those of hydrogen sulphide, the degree of first-stage hydrolysis is somewhat less, 86% and not 100%. Ammonium carbonate solution is also an ammonium buffer mixture, but of somewhat lower pH (about 9.13), because in this case the NH_4^+ ion concentration is higher than the NH_4OH concentration.

These data are of interest in analysis, and have already been used in our discussion of the conditions for precipitation of Groups II and III by their group reagents.

The calculated values of the degree of hydrolysis and pH values of 0.1 *M* solutions of certain salts are given in Table 15.

45. Amphoteric Compounds

We know from inorganic chemistry that the hydroxides of typical metals are bases. Conversely, the hydroxides of nonmetals and of certain less typical metals in the highest oxidation states (for example, chromium and manganese) belong to the acid class. There are also some hydroxides which combine the properties of acids and bases. Such compounds are known as *amphoteric*, and the effect itself as *amphoterism*.

We will often meet amphoteric behaviour in our study of the cations of Groups III-V, and it is important in analysis.

An example of an amphoteric hydroxide is zinc hydroxide.

This hydroxide exhibits a basic character because, like other bases, it dissolves in acids to form the corresponding salts, for example

$$Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O$$

or

$$Zn(OH)_2 + 2H^+ = Zn^{++} + 2H_2O$$

However, $Zn(OH)_2$ also dissolves in alkalies to give zincates, such as

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

or

$$Zn(OH)_2 + 2OH^- = ZnO_2^{--} + 2H_2O$$

In this reaction zinc hydroxide acts as an acid; this is more clear if its formula is written as the formula of an acid:

$$H_2ZnO_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

Thus, $Zn(OH)_2$ combines the properties of an acid and a base. i.e., it is a typical amphoteric oxide. Compounds such as $Al(OH)_3$, $Cr(OH)_3$, $Pb(OH)_2$, $Sn(OH)_2$, $As(OH)_3$, etc., like $Zn(OH)_2$, have amphoteric properties.

The salts formed by the action of alkalies on $Al(OH)_3$ and $Cr(OH)_3$ correspond in composition to the compounds $HAlO_2$ and $HCrO_2$, formed by the loss of a water molecule from the hydroxide molecule, and not to the original hydroxides. The reaction equation for $Al(OH)_3$ is

$$H_3AlO_3 + NaOH = NaAlO_2 + 2H_2O$$

or

$$H_3AlO_3 + OH^- = AlO_2^- + 2H_2O$$

Since amphoteric compounds have both basic and acidic properties, which are attributed to OH^- and H^+ ions respectively, it is reasonable to assume that both kinds of ions are formed simultaneously by the dissociation of amphoteric hydroxides. For example, in the case of $Zn(OH)_2$ some of the molecules dissociate in accordance with the equation*

$$Zn(OH)_2 \rightleftarrows Zn^{++} + 2OH^-$$

and some in accordance with the equation

$$Zn(OH)_2 \rightleftarrows 2H^+ + ZnO_2^{--}$$

or

$$H_2ZnO_2 \rightleftarrows 2H^+ + ZnO_2^{--}$$

We thus have the following chain of interlinked equilibria:

$$2H^+ + ZnO_2^{--} \overset{\text{I}}{\rightleftarrows} Zn(OH)_2 \overset{\text{II}}{\rightleftarrows} Zn^{++} + 2OH^-$$

With this assumption it is easy to explain why $Zn(OH)_2$ dissolves both in acids and in alkalies. When we introduce OH^- ions with an alkali we remove H^+ ions derived from $Zn(OH)_2$. The solution then becomes unsaturated with respect to $Zn(OH)_2$ and the precipitate dissolves with formation of more ZnO_2^{--} ions, i.e., with the formation of zincate.

On the other hand, the effect of an acid is to remove OH^- ions and to dissolve the precipitate with formation of Zn^{++} cations, i.e., of the zinc salt of the acid added.**

From this it follows that *zinc is present mainly as* Zn^{++} *cations in acid solutions, and as* ZnO_2^{--} *anions in alkaline solutions.* Therefore if we want to convert ZnO_2^{--} anions into Zn^{++} cations we must acidify the solution. First a precipitate of $Zn(OH)_2$ is formed, and

---

* For the sake of simplicity the equations for stepwise dissociation of $Zn(OH)_2$ in both cases are not written here, as they should be in a more detailed examination of this question.

** Obviously the addition of H^+ ions also shifts the first equilibrium to the right, while OH^- ions shift the second equilibrium to the left.

then it dissolves in excess acid:

$$ZnO_2^{--} + 2H^+ = \downarrow Zn(OH)_2$$

$$Zn(OH)_2 + 2H^+ = Zn^{++} + 2H_2O$$

Adding the two equations, we obtain the overall equation for the reaction:

$$ZnO_2^{--} + 4H^+ \rightleftarrows Zn^{++} + 2H_2O \qquad (1)$$

However, we have just seen that when alkalies, which remove H^+ ions, act on $Zn(OH)_2$, ZnO_2^{--} ions are formed (with excess alkali). Therefore reaction (1) is reversible and must lead to chemical equilibrium. It is clear from this that *solutions of zinc salts, under any conditions, must contain both* Zn^{++} *cations and* ZnO_2^{--} *anions, and the ratio of their concentrations is determined by the hydrogen ion concentration.* If we apply the law of mass action to this equilibrium, we can write

$$\frac{[Zn^{++}]\cdot[H_2O]^2}{[ZnO_2^{--}]\cdot[H^+]^4} = K_1$$

Since $[H_2O]$ is practically constant, we take it over to the right-hand side of the equation:

$$\frac{[Zn^{++}]}{[ZnO_2^{--}]} = \frac{K_1}{[H_2O]^2}\cdot[H^+]^4$$

Putting

$$\frac{K_1}{[H_2O]^2} = K$$

we finally have

$$\frac{[Zn^{++}]}{[ZnO_2^{--}]} = K\cdot[H^+]^4 \qquad (2)$$

Equation (2) shows that the Zn^{++} ion concentration must rise very rapidly, with a corresponding fall of ZnO_2^{--} concentration, with increase of the H^+ ion concentration. Addition of alkali produces the reverse changes.

All that has been said above about zinc hydroxide is equally applicable to all other amphoteric hydroxides.

According to this theory, every amphoteric hydroxide exhibits two types of dissociation; therefore we must distinguish between their acidic (K_{acid}) and basic (K_{base}) dissociation constants. Comparison of the two constants shows whether a given hydroxide has stronger acidic or basic properties. For example, if we compare K_{acid} and K_{base} for the first-stage dissociation of lead hydroxide

$$K_{base} = \frac{[Pb(OH)^+]\cdot[OH^-]}{[Pb(OH)_2]} = 1\times10^{-3}$$

and

$$K_{acid}=\frac{[HPbO_2^-]\cdot[H^+]}{[H_2PbO_2]}=1\times10^{-11}$$

we find that the basic properties of $Pb(OH)_2$ are much more pronounced than the acidic. In the case of $As(OH)_3$, $K_{acid} = 6 \times 10^{-10}$ and $K_{base} = 1 \times 10^{-14}$, i.e., the acidic properties are the more pronounced.

Examples of amphoteric electrolytes, with equally strong acidic and basic properties, are water and gallium hydroxide, $Ga(OH)_3$. The values of K_{acid} and K_{base} of the latter are almost equal (5×10^{-11} and 2×10^{-11}).

Sparingly soluble hydroxides are precipitated at definite OH^- ion concentrations, i.e., at definite pH, which depends on the solubility product of the hydroxide and the concentration of the metal ions. For example, it was shown in Sec. 26 that when the Mg^{++} concentration is 1×10^{-2} g-ion/litre the precipitation of $Mg(OH)_2$ begins at pH = 9.3 and is practically complete at pH = 11.3. The precipitation of Mg^{++} is even more complete at higher pH values. The addition of excess alkali does not produce any undesirable effects (apart from an increase of the salt effect). On the other hand, we have just seen that in the case of amphoteric hydroxides an excess of alkali dissolves the precipitate. Therefore an amphoteric hydroxide is precipitated within a limited range of pH values. For example, at pH $\approx$ 5 the precipitation of $Al(OH)_3$ is practically complete, while at pH $\approx$ 10 the precipitate begins to dissolve with formation of AlO_2^-. This means that for separation of Al^{+++} as the hydroxide the solution pH must be kept within the range of 5-10. Any reagent giving a pH value in this range must evidently precipitate aluminium hydroxide. For example, we saw earlier that $Al(OH)_3$ can be precipitated from acid solutions by the action of $(NH_4)_2S$, as S^{--} anions bind H^+ ions and the pH of the solution reaches the required value ($\sim$ 9.2). The same applies to precipitation by other salts of weak acids, such as Na_2CO_3, Na_2SO_3, $Na_2S_2O_3$, KCN, etc.

On the other hand, to obtain aluminium hydroxide from a strongly alkaline solution (pH > 10) the pH must be lowered by removal of OH^- ions. This removal can be effected by means of NH_4^+ ions as well as by H^+ ions. Therefore if an excess of NH_4Cl, forming an ammonium buffer mixture (of pH $\approx$ 9) with the alkali, is added to an aluminate solution, $Al(OH)_3$ is precipitated. The reaction can be represented by the equations:

$$AlO_2^- + 2H_2O \rightleftarrows Al(OH)_3 + OH^-$$
$$OH^- + NH_4^+ = NH_4OH$$
$$\overline{AlO_2^- + NH_4^+ + 2H_2O = \downarrow Al(OH)_3 + NH_4OH}$$

The equations show that the reaction essentially involves a shift of the hydrolysis equilibrium of the aluminate as the result of removal of OH^- ions by NH_4^+ ions.

We saw earlier that the basic, acidic, or amphoteric properties of hydroxides are determined by the type of their dissociation. For example, if a hydroxide dissociates forming OH^- ions it is a base; if the dissociation yields H^+ ions it is an acid. If both kinds of ions are formed, the hydroxide is amphoteric. How can we explain the different types of dissociation of different hydroxides?

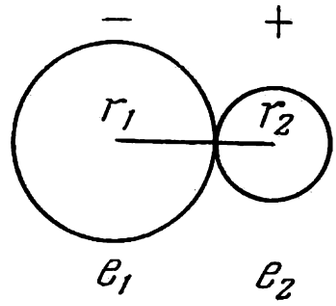


Fig. 26. Schematic structure of a molecule formed by combi nation of two ions

The answer to this question is given by Kossel's theory, according to which hydroxide molecules are conventionally regarded as consisting of ions attracting each other in accordance with Coulomb's law. If the ionic charges are e_1 and e_2 and the radii are r_1 and r_2 (Fig. 26), the force of attraction between them (in a vacuum) is

$$f = \frac{e_1 \cdot e_2}{(r_1 + r_2)^2}$$

The smaller this value, the less strong is the bond between the ions and the more easily is this bond broken when the substance is dissolved in water.

It is clear from this that in the NaOH molecule (shown schematically in accordance with the Kossel theory in Fig. 27) the least stable bond is the one between the Na^+ and O^{--} ions, as the radius of the Na^+ ion is much greater than that of H^+. Therefore the dissociation of NaOH when it is dissolved in water occurs at this weakest bond (i.e., with formation of Na^+ and OH^- ions).

Turning to magnesium hydroxide, we note that the Mg^{++} ion has two positive charges. Moreover, the radius of the Mg^{++} ion ($0.78 \times \times 10^{-8}$ cm) is less than that of Na^+ (0.98×10^{-8} cm). Because of all this, the bond between the oxygen and metal ions is stronger in the $Mg(OH)_2$ molecule than in NaOH. At the same time, the bond between H^+ and O^{--} ions should be weaker in the magnesium hydroxide molecule than in NaOH. Not only are the H^+ ions attracted by O^{--} ions; they are also repelled by the similarly charged metal ions. Whereas the force of attraction between the H^+ and O^{--} ions is the same in both cases, the repulsion force should be greater in the case of $Mg(OH)_2$ because the Mg^{++} ion has a larger charge and smaller radius than Na^+. However, it is still easier to remove an OH^- ion than an H^+ ion from the magnesium hydroxide molecule. Therefore this compound is a base, although a much weaker one than NaOH.

The charges of positive ions formed by successive elements in the same horizontal period of the periodic system (Al, Si, P, S and Cl) gradually increase (from +3 for aluminium to +7 for chlorine) and

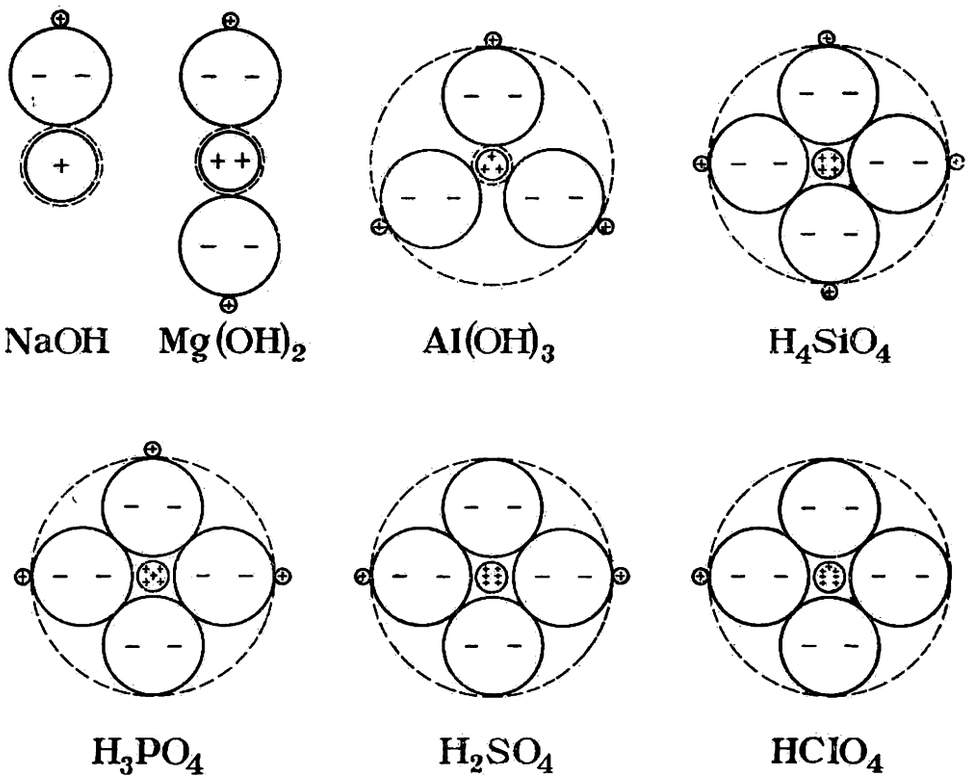


Fig. 27. Structure of hydroxide molecules and their types of dissociation

this trend also persists in other ways, so that the removal of OH^- ions becomes more difficult and the removal of H^+ ions is progressively easier in the hydroxides of this series. Whereas it is easier to detach an OH^- ion than an H^+ ion from an NaOH or $Mg(OH)_2$ molecule, in the case of the $Al(OH)_3$ molecule approximately the same amount of work is needed to detach either; this accounts for the amphoteric properties of $Al(OH)_3$.

In the case of the $Si(OH)_4$ molecule it is easier to detach an H^+ ion than OH^-, so that this compound is an acid, although a very weak one. The removal of H^+ ions is still easier in hydroxides of the elements beyond silicon in the series and their acid-type dissociation increases.

Amphoteric compounds may also be considered in relation to complex formation, as it could be assumed that when an amphoteric hydroxide dissolves in an alkali its molecules combine with OH^- ions of the alkali to form complex ions, e.g.:

$$Zn(OH)_2 + 2NaOH \rightleftarrows Na_2[Zn(OH)_4]$$

or

$$Zn(OH)_2 + 2OH^- \rightleftarrows [Zn(OH)_4]^{--}$$

Similarly, the fact that $Al(OH)_3$ dissolves in alkalies can be attributed to formation of the complex ion $[Al(OH)_4]^-$:

$$Al(OH)_3 + OH^- \rightleftarrows [Al(OH)_4]^-$$

Note that the ions $[Zn(OH)_4]^{--}$, $[Al(OH)_4]^-$, etc., differ from ZnO_2^{--} and AlO_2^- only in their water content, and are really the hydrates of ZnO_2^{--} and AlO_2^-. Thus

$$ZnO_2^{--} + 2H_2O = [Zn(OH)_4]^{--}$$
$$AlO_2^- + 2H_2O = [Al(OH)_4]^-, \text{ etc.}$$

Since ion hydration is not taken into account in the formulas used in this book, we will represent these ions as AlO_2^-, ZnO_2^{--}, etc.

QUESTIONS AND PROBLEMS

1. Calculate (a) the dissociation constant and (b) the ionic product of water at 0°, given that the H^+ and OH^- concentrations at that temperature are $3.6 \times \times 10^{-8}$ g-ion/litre and 1 litre of water weighs 999.9 g.

Answer. $K = 2.3 \times 10^{-17}$; $K_{H_2O} = 1.3 \times 10^{-15}$.

2. Find the pH of solutions containing (a) 2×10^{-4} g-ion H^+ per litre: (b) 0.008 g-ion OH^- per litre.

Answer. (a) 3.70; (b) 11.90.

3. The pH values of two solutions are (a) 2.63; (b) 12.45. Find the H^+ and OH^- ion concentrations in these solutions.

Answer. (a) $[H^+] = 2.34 \times 10^{-3}$; $[OH^-] = 4.27 \times 10^{-12}$.
(b) $[H^+] = 3.54 \times 10^{-13}$; $[OH^-] = 2.82 \times 10^{-2}$.

4. Find the pH of (a) 0.005 *N* HCl; (b) 0.015 *N* KOH.

Answer. (a) 2.30; (b) 12.18.

5. Find the pH of (a) 0.02 *N* CH_3COOH ($K = 1.8 \times 10^{-5}$); (b) 0.05 *N* NH_4OH ($K = 1.8 \times 10^{-5}$).

Answer. (a) 3.22; (b) 10.98.

6. Find the changes of the pH of 0.1 *N* HCl and KOH solutions as the result of hundredfold dilution.

7. What are buffer solutions? List the types of buffer solutions which you know.

8. Find the changes in the pH of a solution containing NaOH in 1×10^{-5} *M* concentration on addition of 0.001 mole of (a) NaOH; (b) HCl to 1 litre of the solution.

Answer. (a) Increased by approximately 2; (b) decreased by 6.

9. A solution contains 0.056 mole of NH_4OH and 0.1 mole of NH_4Cl per litre. Find the pH of this solution and calculate how much it will change on addition of (a) 0.001 mole of NaOH; (b) 0.001 mole of HCl to 1 litre of it. (Compare your answer with the result of the previous problem.)

Answer. pH = 9.00; (a) increased by 0.01; (b) decreased by 0.01.

10. Calculate the pH of buffer solutions containing (a) 0.01 *M* CH_3COOH and 0.01 *M* CH_3COOK; (b) 0.01 *M* CH_3COOH and 0.5 *M* CH_3COOK; (c) 0.5 *M* CH_3COOH and 0.01 *M* CH_3COOK.

Answer. (a) 4.73; (b) 6.43; (c) 3.03.

11. A formate buffer mixture is prepared from 100 ml of 23 *N* formic acid, HCOOH, and 3 ml of 15 *N* NH_4OH. Calculate the pH of the mixture.

Answer. pH = 2.05.

12. What is hydrolysis? When and why is the reaction of a salt solution (a) neutral; (b) acid; (c) alkaline?

13. How does the hydrolysis of salts of (a) polybasic acids and (b) multivalent metals differ from the hydrolysis of salts of monobasic acids and univalent metals?

14. List the hydrolysis products of salts in relation to the valencies of their constituent cations and anions. In particular, discuss the hydrolysis of salts of the following types: $Me^{+}A^{-}$, $Me_2^{+}A^{--}$, $Me_3^{+}A^{---}$, $Me^{++}A^{--}$ and $Me^{+++}A_3^{-}$, illustrating your answer by the hydrolysis equations.

15. Why cannot the hydrolysis of Na_2CO_3 be represented by the overall equation

$$Na_2CO_3 + 2H_2O \rightleftarrows 2NaOH + H_2CO_3?$$

In what cases is it permissible to add the equations for the separate hydrolysis stages?

16. Explain why Na_2CO_3 precipitates manganese carbonate from solutions of manganese salts and aluminium hydroxide from solutions of aluminium salts. Write the equations for the reactions.

17. By what means can hydrolysis be (a) intensified; (b) suppressed? What is the purpose of suppressing the hydrolysis of the group reagents for Groups II and III and how is it achieved?

18. Calculate the hydrolysis constants (for all stages) of the following salts: (a) NH_4Cl; (b) NH_4CN; (c) $(NH_4)_2CO_3$; (d) Na_3PO_4.

Answer. (a) 5.6×10^{-10}; (b) 0.78; (c) 10; 1.3×10^{-3}; (d) 4.5×10^{-2}; 1.6×10^{-7}; 1.3×10^{-12}.

19. Calculate the degree of hydrolysis of each of the salts in the previous example, taking (where necessary) the salt concentration as 0.1 *M*.

Answer. (a) 0.0074%; (b) 46.8%; (c) 76.0%; 3.5%; (d) 67.4%; 0.1%; 0.0004%.

20. What is an amphoteric compound? How does the amphoteric hydroxide $Pb(OH)_2$ dissociate into ions? What is the action of acids and alkalies on it? Write the equations for the reactions.

21. How can AlO_2^{-} anions be converted into Al^{+++} cations?

22. Explain the basic, amphoteric and acidic nature of hydroxides with the aid of Kossel's theory.

46. Double and Complex Salts

In addition to salts of the usual type, such as $Al_2(SO_4)_3$, $FeSO_4$, $Fe(CN)_2$, etc., in studying the reactions of the cations of Group III and the subsequent groups we shall meet compounds of more complex composition. These include ordinary (aluminium) alum $KAl(SO_4)_2 \cdot 12H_2O$, chrome alum $KCr(SO_4)_2 \cdot 12H_2O$, Mohr's salt $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, potassium ferrocyanide $K_4[Fe(CN)_6] \cdot 3H_2O$, etc.

Molecules of these substances are formed by combination of molecules of simpler salts; for example

$$K_2SO_4 + Al_2(SO_4)_3 = 2KAl(SO_4)_2$$
$$(NH_4)_2SO_4 + FeSO_4 = (NH_4)_2Fe(SO_4)_2$$
$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6]$$

They are therefore known as *compounds of higher order*. The course of electrolytic dissociation of such compounds is of considerable interest in analysis.

Let us consider some actual examples. Dissolve a small amount of Mohr's salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, in water and test the solution for Fe^{++} by the action of $(NH_4)_2S$:

$$FeSO_4 + (NH_4)_2S = \downarrow FeS + (NH_4)_2SO_4$$

or

$$Fe^{++} + S^{--} = \downarrow FeS$$

A black precipitate of FeS indicates the presence of the Fe^{++} ion. This test shows that Fe^{++} ions are present in a solution of Mohr's salt. Similarly, a solution of Mohr's salt gives the tests for NH_4^+ with caustic soda (evolution of NH_3 on heating), and for SO_4^{--} with barium chloride (precipitation of $BaSO_4$).

From all this we may conclude that Mohr's salt dissociates in accordance with the equation

$$(NH_4)_2Fe(SO_4)_2 = 2NH_4^+ + Fe^{++} + 2SO_4^{--}$$

The dissociation of alum is similar:

$$KAl(SO_4)_2 = K^+ + Al^{+++} + 2SO_4^{--}$$

Therefore *when these salts dissociate they yield the ions present in the simple salts from which they were formed, i.e., they act as mixtures of simple salts.* Such compounds are known as *double salts.*

However, compounds of higher order do not always dissociate as shown in these examples. For instance, we may consider potassium ferrocyanide, $K_4[Fe(CN)_6]$. On addition of $NaHC_4H_4O_6$ to a solution of this salt a characteristic white crystalline precipitate of $KHC_4H_4O_6$ is formed. This proves the presence of K^+ in solution. However, when $(NH_4)_2S$ is added to another portion of the solution FeS is not precipitated. The test for CN^- also fails. At the same time a solution of $K_4[Fe(CN)_6]$ gives a number of other reactions not given by either Fe^{++} or CN^- separately. For example, a fine dark blue precipitate of Prussian blue,* $Fe_4[Fe(CN)_6]_3$, is formed on addition of $FeCl_3$. The equation for this reaction is

$$4FeCl_3 + 3K_4[Fe(CN)_6] = \downarrow Fe_4[Fe(CN)_6]_3 + 12KCl$$

All these facts show that a solution of $K_4[Fe(CN)_6]$ does not contain any** Fe^{++} or CN^- ions, but complex $[Fe(CN)_6]^{==}$ ions are present; these have their own characteristic reactions, differing from the reactions of Fe^{++} and CN^-. Therefore the dissociation of $K_4[Fe(CN)_6]$ is represented by the equation

$$K_4[Fe(CN)_6] = 4K^+ + [Fe(CN)_6]^{==}$$

---

* Used as a blue water-colour.

** More correctly, it contains *hardly any* Fe^{++} or CN^- ions. It will be shown later that complex ions can dissociate into their constituent simple ions, but the degree of this dissociation is usually very low.

This is confirmed by electrolysis of this salt; iron in the form of the complex ion $[Fe(CN)_6]^{=}$ moves to the anode and not the cathode.

To represent these properties in the formula of the salt, it is written as $K_4[Fe(CN)_6]$, with the group of atoms forming the complex enclosed in square brackets.

Salts such as $K_4[Fe(CN)_6]$, the formation of which involves complexes which do not exhibit characteristic reactions of the constituent simple ions, belong to the class of *complex compounds*. In addition to complex salts, this class includes complex acids and bases and also certain nonelectrolytes.

While the complex ion $[Fe(CN)_6]^{=}$ is a combination of a positive Fe^{++} ion with six negative CN^- ions, in other cases complexes may contain neutral molecules of NH_3, H_2O and certain other substances instead of negative ions.

For example, when ammonia is added to $AgNO_3$ solution, the following reaction occurs:

$$AgNO_3 + 2NH_4OH = [Ag(NH_3)_2]NO_3 + 2H_2O$$

or

$$Ag^+ + 2NH_4OH = [Ag(NH_3)_2]^+ + 2H_2O$$

The effect of the formation of the $[Ag(NH_3)_2]^+$ complex is that certain reactions for the Ag^+ ion no longer work. If a chloride is added to the $[Ag(NH_3)_2]NO_3$ solution, AgCl is not precipitated. Similarly, Ag_3PO_4 and $AgBrO_3$ are not precipitated by Na_2HPO_4 and $KBrO_3$, etc.

Complex salts are of great importance in analysis, and we will therefore consider them in more detail.

47. Structure of Complex Compounds

According to Werner's *coordination theory* (1893), a positive ion termed the *central ion* or *complex-former* usually occupies the central position in the molecule of a complex compound. It is coordinated or linked to *ligands*, which are negative ions or neutral molecules in its immediate vicinity. The central ion with its ligands constitutes the *inner coordination sphere* of the compound. In most cases there is also an *outer coordination sphere* consisting of negative or positive ions.

The ions of the outer sphere are linked to the central ion by *ionic bonds*, i.e., when the substance is dissolved in water they split off as free ions. On the other hand, the bonds between the central ion and the ligands are *nonionic* and therefore the inner coordination sphere is hardly dissociated at all when the compound is dissolved in water. For example, in $K_4[Fe(CN)_6]$ the central ion is Fe^{++} and the

ligands are CN^- ions. The outer coordination sphere contains K^+ ions. The $[Fe(CN)_6]$ group, enclosed in square brackets, is the inner coordination sphere, which forms the complex ion $[Fe(CN)_6]^{=}$ when the compound is dissolved in water.

The charge of a complex ion is the algebraic sum of the charges of the central ion and the ligands. For example, the charge of the $[Fe(CN)_6]^{=}$ ion is $(+2) + (-6) = -4$.

If the ligands are neutral molecules, the charge of the complex is the same as that of the central ion; for instance, the charge of the $[Ag(NH_3)_2]^+$ ion is the same as that of the Ag^+ ion.

The charge of the complex may also be deduced from the composition of the outer coordination sphere. When the charge of the complex has been found, it is easy to calculate the charge of the central ion if it is not known. For example, the complex compound $Na_3[Co(NO_2)_6]$ has three singly-charged positive Na^+ ions in the outer sphere. Since all molecules are electrically neutral, the charge of the $[Co(NO_2)_6]^{---}$ complex must be -3. However, as the NO_2^- ions, which are the ligands, have a total of six negative charges, the charge of the central ion must be $+3$.

The total number of ligands coordinated by a given central ion in a complex is the *coordination number of the central ion.* The coordination number of most complex-formers (Cr^{+++}, Co^{+++}, Fe^{++}, Fe^{+++}, Zn^{++}, Ni^{++}, Pt^{++++}, etc.) is 6. The coordination number of Cd^{++}, Cu^{++}, Hg^{++}, Pt^{++} and certain other ions is 4. Other coordination numbers are also known, e. g., 2, 3, 8, etc.

The coordination number plays a part of no less importance than the valency of atoms or ions in the chemistry of complex compounds. The practical significance of coordination numbers is similar to that of valencies, since a knowledge of coordination numbers makes it possible to write the formulas of various complex compounds.

For example, if we know that the coordination number of the Cd^{++} ion is 4 we can conclude that complex ammines formed by this ion should have formulas such as

$$[Cd(NH_3)_4]Cl_2,\ [Cd(NH_3)_4]SO_4,\ [Cd(NH_3)_4](OH)_2,\ \text{etc.}$$

Similarly, complex cyano compounds of cadmium should have formulas like

$$K_2[Cd(CN)_4],\ Na_2[Cd(CN)_4]$$

etc., as the corresponding complex ion, containing a positive bivalent Cd^{++} ion and four negative univalent CN^- ions, should be an anion with two negative charges.

It should be remembered that under certain conditions the maximum coordination number characteristic for a given complex-former may not be reached, and the so-called *coordination-unsaturated* compounds are then formed.

It was shown by A. K. Babko that one very important condition for this is the concentration of the reacting substances. For example, in the reaction between ferric salts and thiocyanates (salts of HCNS) the $[Fe(CNS)_6]^{---}$ complex, corresponding to the maximum coordination number of the Fe^{+++} ion, is formed only in the presence of a very large excess of CNS^- ions. At lower CNS^- concentrations various coordination-unsaturated compounds are formed; the lowest coordination number (1) is found in the complex $[Fe(CNS)]^{++}$.

Most ligands, including all univalent negative ions and molecules such as NH_3, H_2O, C_2H_5OH (ethyl alcohol), C_5H_5N (pyridine), etc., can occupy only single coordination positions in a complex. However, certain ligands can occupy two such positions. These include the molecules of hydrazine $H_2N—NH_2$ and ethylenediamine $H_2N—CH_2—CH_2—NH_2$, the bivalent ions $C_2O_4^{--}$, CO_3^{--}, SO_4^{--}, etc. All such bidentate ligands are linked to the complex-forming ion at two points; for example, a hydrazine molecule is linked by both its nitrogen atoms.

The tendency to form complexes is most pronounced in elements in the middle of the long periods of the Mendeleyev periodic system, and especially Group VIII elements. The cations of these metals most frequently act as complex-formers and give rise to a great variety of complex compounds.

The formation of complex compounds, which does not conform to the usual concepts of valency, may be interpreted in various ways in the light of the electronic theory of the structure of matter.

It may be regarded as the result of electrostatic attraction forces acting between the ligands and the complex-forming ion. It must be remembered that electrostatic attraction forces always exist between opposite charges, whether these charges are equal in magnitude or not. For example, the Fe^{++} ion can attract two CN^- ions to form an electrically neutral molecule of $Fe(CN)_2$; but even after this has been formed, the positively charged Fe^{++} ion retains its ability to attract oppositely charged (negative) ions. Therefore if an Fe^{++} cation meets an *excess* of CN^- anions in solution it should attract all such anions in its vicinity, and not merely two. However, it can only hold a limited number, because the number of positions which the CN^- ions can occupy in close enough proximity to the Fe^{++} ion is limited.

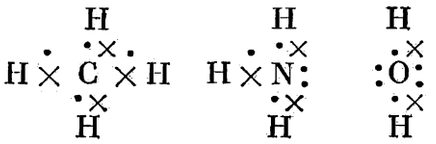
On the other hand the CN^- ions, which are attracted to Fe^{++}, are mutually repelled because of their like charges. The greater the number of CN^- ions attached to an Fe^{++} ion, the greater do these repulsion forces become. It is clear that eventually they must exceed the forces of attraction between the Fe^{++} and CN^- ions and no more of the latter can then become attached. In the present instance this

occurs when six CN^- ions are attached to the Fe^{++} ion, i.e., when the complex $[Fe(CN)_6]^{=}$ has been formed.

Ligands which are neutral molecules of NH_3, H_2O and similar substances are attached to the central ion by virtue of being dipoles; they are therefore oriented in a definite manner with respect to the central ion and are attracted by it.*

It is more probable, however, that such complexes are formed as the result of a special type of covalent bonding between the central ion and the ligands.

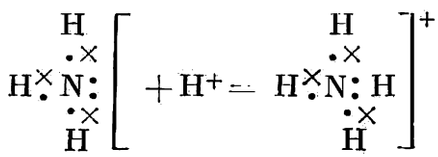
We know from the course of general chemistry that a covalent bond is formed by sharing electron pairs between atoms; for example



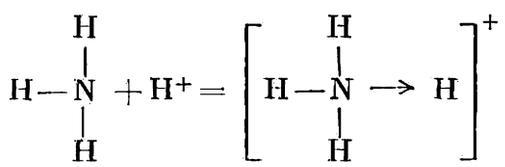
In the schemes above the electrons supplied by hydrogen atoms for such pairs are indicated by crosses, those from the other atoms, by dots. These schemes show that each of the atoms contributes one electron to a shared pair.

However, shared electron pairs may also arise in another way, from one of the atoms only. For example, an ammonia molecule, which has a "lone pair" of electrons (belonging to the nitrogen atom only), can share these electrons with an H^+ ion.

An ammonium ion is then formed; like the ammines, it may be regarded as a complex. The formation of the ammonium ion can be represented schematically as follows:

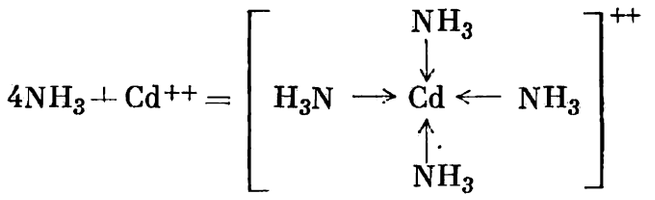


A bond of this type, effected by the sharing of an electron pair supplied by one of the atoms, is known as a coordinate or "donor-acceptor" bond. The atom supplying the electron pair is known as the *donor*, while the other atom is the *acceptor*. A coordinate bond is schematically represented by an arrow (→) directed from the donor to the acceptor. With this notation the above scheme is written as follows:



* See the discussion of solvate and hydrate formation in Sec. 11.

Other complexes are formed as the result of coordinate bonding between atoms; for example:



The formation of various crystalline hydrates, which by their properties belong to the typical complex compounds, may be explained similarly. Typical examples* are

$$[Cr(OH_2)_6]Cl_3,\ [Co(OH_2)_6](NO_3)_2,\ [Cu(OH_2)_4]SO_4 \cdot OH_2$$

Very many complex compounds are known; as was pointed out by D. I. Mendeleyev in his time, the study of these compounds is of very great scientific and practical significance. Following the precepts of this great scientist and thinker, the eminent chemists L. A. Chugaev and N. S. Kurnakov devoted a series of remarkable researches to this problem.

48. Stability of Complexes

Compounds of higher order are subdivided into double salts and complex compounds, in accordance with the nature of their dissociation and their behaviour in analytical reactions. However, a closer study of the matter shows that a sharp boundary cannot be drawn between double salts and complex compounds.

For example, it has been proved experimentally that fairly concentrated solutions of double salts contain complex as well as simple ions; for example, a solution of Mohr's salt contains $[Fe(SO_4)_2]^{--}$ ions. On the other hand, complex ions are also capable of dissociating into simple ions, as can be easily shown by the following experiments.

Add NH_4OH solution to a solution of $AgNO_3$ until the liquid smells of ammonia. As already stated, the complex salt $[Ag(NH_3)_2]NO_3$ is formed, and therefore $AgBrO_3$ and AgCl are not precipitated when $KBrO_3$ and KCl are added to the solution. Now act on separate portions of the $[Ag(NH_3)_2]NO_3$ solution with KBr, KI and H_2S. These are reagents for Ag^+, giving precipitates of AgBr (yellowish), AgI (yellow) and Ag_2S (black) with silver ions. It is found that a solution of $[Ag(NH_3)_2]NO_3$ also gives these reactions.

---

* In crystalline hydrates the bonding between the complex-former and water molecules is effected through the oxygen atoms; it is therefore usual to represent water as OH_2 in such cases.

Thus, while in the first two reactions $[Ag(NH_3)_2]NO_3$ exhibits the typical properties of a complex salt, in the last three it acts like a double salt.

These facts evidently indicate that a solution of $[Ag(NH_3)_2]NO_3$ contains Ag^+ ions in addition to complex $[Ag(NH_3)_2]^+$ ions. However, the silver ion concentration is so low that only the solubility products of the least soluble salts such as AgBr, AgI and Ag_2S are reached, whereas those of the more soluble $AgBrO_3$ and AgCl are not. It follows that the complex salt dissociates by stages:

first stage

$$[Ag(NH_3)_2]NO_3 \longrightarrow [Ag(NH_3)_2]^+ + NO_3^- \quad (1)$$

second stage

$$[Ag(NH_3)_2]^+ \rightleftarrows Ag^+ + 2NH_3 \quad (2)$$

The first-stage dissociation is of the strong electrolyte type, i.e., complete, while the second-stage dissociation is slight and may be represented by a certain constant*:

$$\frac{[Ag^+]\cdot[NH_3]^2}{[Ag(NH_3)_2]^+} = K_{inst} = 6.8 \times 10^{-8}$$

The higher this constant, the more does the complex dissociate and the less stable it is. It is known as the *instability constant* of the complex. Instability constants of the most important complexes are given in Table V (see Appendix).

Table V shows that the instability constants of different complexes differ greatly.

For example, the instability constant of the complex $[Ag(S_2O_3)]^-$ is 1×10^{-13} and that of $[Ag(CN)_2]^-$ is 1×10^{-21}. Therefore $[Ag(NH_3)_2]^+$ is the least stable and $[Ag(CN)_2]^-$ is the most stable of the three silver complexes listed.

If we know the instability constant of a complex, we can calculate theoretically the concentration of the corresponding simple ion in a solution of a complex salt. This is illustrated by the following numerical examples.

Example 1. Calculate the Ag^+ ion concentration in 0.01 *M* solutions of (a) $[Ag(NH_3)_2]NO_3$ and (b) $K[Ag(CN)_2]$.

Solution. Denote the required Ag^+ ion concentration by x; the equation for dissociation of the $[Ag(NH_3)_2]^+$ complex gives

$$[NH_3] = 2x \text{ and } [Ag(NH_3)_2]^+ = 0.01 - x \approx 0.01$$

since the degree of dissociation of the complex is slight. Therefore we can write

$$K_{inst} = \frac{x\cdot(2x)^2}{0.01} = 6.8\cdot10^{-8}$$

* The molar concentration of the complex ion is indicated by its formula in square brackets.

and hence

$$x = [Ag^+] = \sqrt[3]{\frac{6.8 \times 10^{-10}}{4}} = 5.5 \times 10^{-4} \text{ g-ion/litre}$$

The calculation for the $[Ag(CN)_2]^-$ complex is similar:

$$K_{inst} = \frac{x \cdot (2x)^2}{0.01} = 1 \times 10^{-21}$$

and

$$x = [Ag^+] = \sqrt[3]{\frac{1 \times 10^{-23}}{4}} = 1.4 \times 10^{-8} \text{ g-ion/litre}$$

These numerical examples show that the higher the instability constant of a complex, the greater is the concentration of the corresponding simple ion at a given molar concentration of the complex. For example, the $[Ag(NH_3)_2]NO_3$ complex, having the higher instability constant (6.8×10^{-8}), contains about 40,000 as much Ag^+ ions in a 0.01 *M* solution as the $K[Ag(CN)_2]$ complex with its considerably lower K_{inst} (1×10^{-21}). This difference in Ag^+ ion concentrations must, of course, influence analytical reactions. It is to be expected that the number of different precipitation reactions of the Ag^+ ion should decrease with decreasing Ag^+ concentration, because the number of cases where the solubility products of the sparingly soluble silver salts become unattainable must increase.

These theoretical considerations are fully confirmed by experiment. This is shown in Table 16, where the effects of the various reagents for Ag^+ on solutions of different complex salts of silver are compared.

It follows that *the behaviour of a complex salt in precipitation reactions is determined primarily by the ratio between the instability constant of the complex and the solubility product of the precipitated compound. The probability of precipitation increases with increasing* K_{inst} *and decreasing solubility product.*

The course of a precipitation reaction may also be strongly influenced by the presence of excess ions (or undissociated molecules) which are present as ligands in the complex. For example, when $Na_2S_2O_3$ is added to a solution of the complex salt $Na[AgS_2O_3]$ the common $S_2O_3^{--}$ ions lower the degree of dissociation of the complex and therefore decrease the Ag^+ concentration. Calculation shows that it is precisely because a small excess of $Na_2S_2O_3$ is present* that no precipitate is formed with KBr. In the absence of this, excess AgBr would be precipitated. This is illustrated by Example 2.

---

* The excess $Na_2S_2O_3$ is introduced when $Na[AgS_2O_3]$ is formed by the reaction

$$AgNO_3 + Na_2S_2O_3 = Na[AgS_2O_3] + NaNO_3$$

Table 16

Action of Reagents for Ag^+ Ions on Solutions of Simple and Complex Silver Salts*

Reagents for Ag^+	Ions containing Ag in solution			
	Ag^+	$[Ag(NH_3)_2]^+$ $K_{inst}=6.8\times10^{-8}$	$[AgS_2O_3]^-$ $K_{inst}=1\times10^{-13}$	$[Ag(CN)_2]^-$ $K_{inst}=1\times10^{-21}$
$KBrO_3$	White precipitate $AgBrO_3$ $SP=5.8\times10^{-5}$	—	—	—
KCl	White precipitate AgCl $SP=1.5\times10^{-10}$	—	—	—
KBr	Yellowish precipitate AgBr $SP=7.6\times10^{-13}$	AgBr	—	—
KI	Yellow precipitate AgI $SP=1.5\times10^{-16}$	AgI	AgI	—
H_2S	Black precipitate Ag_2S $SP=1.6\times10^{-49}$	Ag_2S	Ag_2S	Ag_2S

* A dash indicates absence of a precipitate.

Example 2. Find by calculation whether AgBr is precipitated when equal volumes of 0.02 *M* solutions of $Na[AgS_2O_3]$ and KBr are mixed (a) in the absence and (b) in the presence of excess $Na_2S_2O_3$.

Solution. When equal volumes of 0.02 *M* solutions of KBr and $Na[AgS_2O_3]$ are mixed, the concentration of each substance is halved to 10^{-2} *M*. Taking this into account and noting that $[Ag^+] = [S_2O_3^{--}] = x$, we have

$$K_{inst}=\frac{[Ag^+]\cdot[S_2O_3^{--}]}{[AgS_2O_3]^-}=\frac{x^2}{10^{-2}}=10^{-13}$$

hence

$$x=3.3\times10^{-8}\ \text{g-ion/litre}$$

Therefore

$$[Ag^+]\cdot[Br^-] = 3.3 \times 10^{-8} \cdot 10^{-2} = 3.3 \times 10^{-10}$$

As this is greater than the solubility product of AgBr (7.7×10^{-13}), AgBr should be precipitated. However, experiment shows that this is not the case. The discrepancy between the theoretical calculation and the experimental result is explained if it is taken into account that $Na[AgS_2O_3]$ solutions always contain excess $Na_2S_2O_3$, which greatly lowers the Ag^+ ion concentration. To verify this explanation, let us calculate the concentration of $S_2O_3^{--}$ ions in solution which would make precipitation of AgBr impossible under the specified conditions. We first find, from the equation for the solubility product of AgBr, the highest Ag^+ ion concentration at which AgBr is still not precipitated:

$[Ag^+]\cdot[Br^-] = 7.7 \times 10^{-13}$ and $[Ag^+] = 7.7 \times 10^{-13} : 0.01 = 7.7 \times 10^{-11}$ g-ion/litre

Then, from the equation for the instability constant of the complex, we find the $S_2O_3^{--}$ ion concentration at which the Ag^+ concentration has this value (7.7×10^{-11} g-ion/litre):

$$\frac{[Ag^+]\cdot[S_2O_3^{--}]}{[AgS_2O_3]^-} = \frac{7.7 \times 10^{-11} \times [S_2O_3^{--}]}{10^{-2}} = 1 \times 10^{-13}$$

and

$$[S_2O_3^{--}] = \frac{1 \times 10^{-15}}{7.7 \times 10^{-11}} = 1.3 \times 10^{-5} \text{ g-ion/litre}$$

This calculation shows that a very slight excess of $Na_2S_2O_3$ is sufficient to prevent precipitation of AgBr. Such an excess is practically always present in solutions of this complex salt. In contrast to silver bromide, the precipitation of silver iodide is prevented only if $Na_2S_2O_3$ is present in sevenfold excess over the concentration of the complex ion (10^{-2} g-ion/litre), while in the case of silver sulphide the required excess is about 9,000-fold.

It is obvious that AgBr is not precipitated when KBr is added to a solution of this complex salt, whereas KI and H_2S precipitate AgI and Ag_2S respectively.

In the above reactions the complexes are decomposed because the complex-forming ion is converted into a sparingly soluble salt. Complexes can also be decomposed by formation of complexes of higher stability. For example, the following reaction occurs when KCN acts on $[Ag(NH_3)_2]Cl$ solution:

$$[Ag(NH_3)_2]Cl + 2KCN = K[Ag(CN)_2] + KCl + 2NH_3$$

or

$$[Ag(NH_3)_2]^+ + 2CN^- = [Ag(CN)_2]^- + 2NH_3$$

Complexes can also be decomposed by binding the ligands present. If an acid such as H_2SO_4 is added to a solution of the dark-blue complex copper salt $[Cu(NH_3)_4]SO_4$ the colour changes to pale blue. This is because the $[Cu(NH_3)_4]^{++}$ ions responsible for the dark-blue colour are decomposed by reaction of the NH_3 molecules with hydrogen ion leading to the formation of the more stable complex NH_4^+ ions; the pale-blue colour of the resultant solution is due to the presence of Cu^{++} ions.

The reaction is

$$[Cu(NH_3)_4]SO_4 + 2H_2SO_4 = CuSO_4 + 2(NH_4)_2SO_4$$

or

$$[Cu(NH_3)_4]^{++} + 4H^+ = Cu^{++} + 4NH_4^+$$

Acidification may also decompose complexes in which the ligands are anions of very weak acids, owing to the formation of undissociated molecules of these acids. For example, this occurs in the case of complexes formed by heavy-metal cations with certain organic compounds of an acidic nature (such as phenols, dimethylglyoxime, dyes of the alizarin type, etc.).

It follows from all this that *there is no difference in principle between double and complex salts.* The two classes of compounds are merely the extreme types of compounds of higher order, which in fact form a complete range from typical double salts, with practically complete dissociation of the complexes, to typical complex salts in which there is virtually no dissociation.

49. Significance of Complex Compounds in Analysis

It has already been stated that as the result of complex formation many ions cease to give their characteristic reactions. This must be taken into account in analysis, as otherwise erroneous results would be obtained.

For example, organic compounds containing $>$CHOH groups in their molecules, such as various sugars, tartaric and citric acids, glycerol, and similar substances form complexes with many cations; as a result, these cations are no longer precipitated by OH^- ions or by certain other reagents used in analysis. Therefore organic substances must be removed from an unknown substance before analysis, especially as they may act as protective colloids and prevent the coagulation of certain precipitates.

As already stated, organic compounds are removed by oxidation, the unknown substance being heated with a mixture of concentrated nitric and sulphuric acids.

However, the formation of complexes may make analysis much easier instead of interfering. The following examples illustrate this.

1. Often the presence of Fe^{+++} ions interferes with detection of other ions, such as Co^{++}, Ti^{++++}, etc. In such cases, instead of removing Fe^{+++} as an insoluble compound such as $Fe(OH)_3$, it is more convenient to bind Fe^{+++} into a stable complex by addition of tartaric or citric acid. This achieves the same effect as precipitation of Fe^{+++}; the concentration of the latter in solution is lowered so much that it no longer interferes with the detection of the ions in

question. Instead of tartaric or citric acid, phosphoric acid or ammonium fluoride may be added, as Fe^{+++} forms the complexes $[Fe(PO_4)_2]^{---}$ and $[FeF_6]^{---}$ with these substances.

2. In systematic analysis of Group IV cations, Cu^{++} and Cd^{++} remain together in solution after separation of the other cations. However, the Cu^{++} ion interferes with the most characteristic reaction of Cd^{++}, the formation of a bright yellow precipitate of CdS with H_2S, as it gives a black precipitate of CuS with H_2S. Therefore Cu^{++} must be removed from the solution in one way or another. For example, Cu^{++} ions can be reduced to metallic copper by the metals Al, Zn or Fe, which do not reduce Cd^{++} in acid solution.

However, it is much simpler to convert Cu^{++} and Cd^{++} ions into the soluble complex cyanides $[Cu(CN)_4]^{---}$ and $[Cd(CN)_4]^{--}$ by addition of KCN to the solution.* The copper ion concentration is then lowered so much that the solubility product of copper sulphide can no longer be reached. On the other hand, the less stable $[Cd(CN)_4]^{--}$ ion yields enough Cd^{++} ions to give a precipitate of CdS with H_2S.

Thus, *the test for* Cd^{++} *with* H_2S, *non-specific in itself, becomes specific in the presence of* KCN.

3. The analysis of Group IV cations can be greatly simplified by addition of glycerol, $CH_2OH—CHOH—CH_2OH$, to a solution containing the cations Cu^{++}, Cd^{++}, Bi^{+++} and Pb^{++}; all these cations with the exception of Cd^{++} form complex ions not precipitated by alkalies with glycerol. If caustic soda is added to the solution containing glycerol, Cd^{++} is separated as $Cd(OH)_2$; the remaining cations can be detected by their characteristic reactions in separate portions of the solution, because the complexes present yield sufficient concentrations of the corresponding simple ions for these reactions (or they can be decomposed by addition of an acid).

This procedure for *suppressing undesirable reactions by means of masking agents which convert interfering ions* (Fe^{+++}, Cu^{++}, *etc.*) *into stable complexes* is frequently used in analysis and is of great practical importance, as it permits the detection of many ions by the fractional method which would otherwise be impossible.

The importance of complex compounds in analysis depends even more on the fact that reactions of complex formation are often highly sensitive and specific tests for individual ions. For example, Fe^{+++} is usually detected by the action of $K_4[Fe(CN)_6]$, which gives Prussian blue $Fe_4[Fe(CN)_6]_3$; Cu^{++} is detected in the form of the complex compounds $Cu_2[Fe(CN)_6]$ or $[Cu(NH_3)_4]SO_4$; Co^{++} is found by the formation of the complex salts $(NH_4)_2[Co(CNS)_4]$ or $Co[Hg(CNS)_4]$;

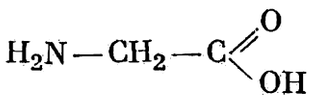
---

* The Cu^{++} ion is reduced to Cu^{+} in the formation of the $[Cu(CN)_4]^{---}$ complex.

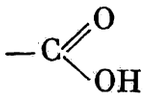
Ni^{++} gives a complex salt with the organic reagent dimethylglyoxime, etc.

The complex compounds formed by various cations with organic reagents usually belong to the class of compounds known as *internally complex salts* and are of great interest in analytical chemistry.

Salt formation by organic compounds depends on the presence in their molecules of certain atomic groups with acidic properties. These include —COOH, —OH, =NOH, =NH, $-NH_2$, $-SO_3H$ and others. Under certain conditions the hydrogen atoms of these groups can be replaced by metal atoms. If the molecule of an organic compound also contains a group which can act as a ligand for the given cation, the latter replaces the hydrogen atom in the acidic group and can also form a coordination bond with the ligand group. An internally complex salt is then formed. The simplest example of an internally complex salt is the copper salt of glycocoll (aminoacetic acid)

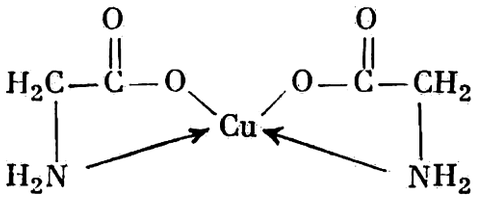


which contains, in addition to the acidic group



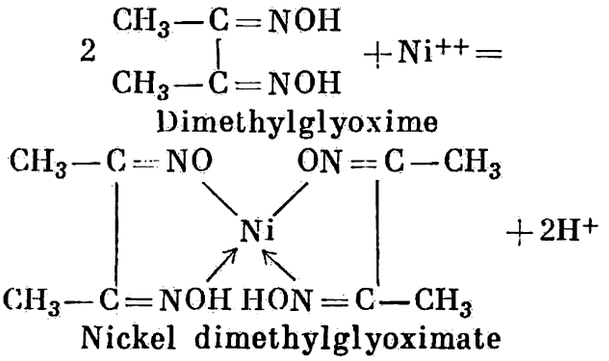
an amino group, H_2N—, which can coordinate to a Cu^{++} ion.

Accordingly, the structure of copper aminoacetate corresponds to the formula



The Cu^{++} ion in this compound has all the properties of an ion with all its coordination sites filled.

A similar internally complex salt is the compound of the Ni^{++} ion with dimethylglyoxime, known as nickel dimethylglyoximate; the reaction by which it is formed can be represented as follows:



Dimethylglyoxime

Nickel dimethylglyoximate

The equation shows that, in addition to replacing two hydrogen atoms of acidic =NOH groups in two molecules of dimethylglyoxime, the Ni^{++} ion also forms coordination bonds with two nitrogen atoms of two more =NOH groups in the same dimethylglyoxime molecules.

It follows from these examples that molecules of internally complex salts have cyclic (ring) structure.* They are of great interest in analytical chemistry because *they are usually only sparingly soluble in water, are brightly coloured, and dissociate only very slightly into ions.*

A very important fact is that the possibility of formation of internally complex salts is often associated with specific and individual properties of the cations; this is not the case in the formation of simple salts. This makes the action of organic reagents more specific.

It is found that Ni^{++} gives characteristic, usually red, precipitates not only with dimethylglyoxime but also with various other organic compounds (dioximes) containing the atomic group

$$\begin{array}{l} -C=NOH \\ \quad | \\ -C=NOH \end{array}$$

in their molecules. This group is therefore *specific for the nickel ion.* There are similar specific groups for many other ions.

Experiment shows that the analytical properties of reagents containing a particular specific group are also influenced to a certain extent by the radicals to which it is linked. Therefore by changing these radicals it is sometimes possible to improve the properties of a reagent considerably and to increase its sensitivity or specificity.

As the number of organic compounds is enormous and the structure and composition of their molecules can be varied by a great variety of methods by introduction of various groups, organic chemistry offers great potentialities to analysis in the search for new specific and highly sensitive reagents for various ions.

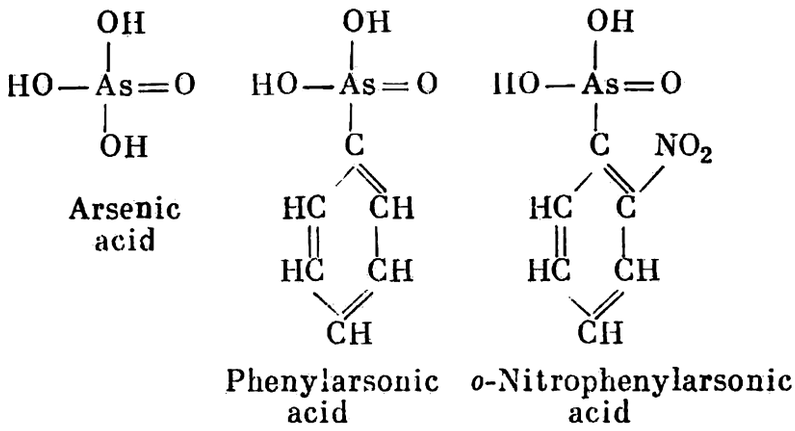
This is illustrated by the following example, taken from the researches of V. I. Kuznetsov and I. P. Alimarin. Arsenic acid precipitates most tri- and quadrivalent cations in acid solution. If one of its hydroxyl groups is replaced by a benzene residue (i.e., the phenyl radical $-C_6H_5$), the result is phenylarsonic acid, which is more selective. In the presence of mineral acids it precipitates only the ions of zirconium, hafnium, tin (IV), niobium, tantalum and (incompletely) titanium. Further if the hydrogen atom in the *ortho* position** in the benzene nucleus of the phenylarsonic acid molecule is replaced by a nitro group ($-NO_2$), the result is *ortho*-nitrophenylarsonic acid, which is a highly

---

* Complex compounds containing rings are known as "chelate" compounds. Internally complex salts belong to this class.

** At the C atom adjacent to the carbon linked to the arsenic acid residue.

specific reagent for Sn^{++++} (this is the only cation precipitated by it in the presence of hydrochloric and tartaric acids):



As was already pointed out in Sec. 8, organic reagents were first used in organic analysis by M. A. Il'insky, who proposed in 1884 the organic compound α-nitroso-β-naphthol as a reagent for the Co^{++} ion (see p. 292). However, organic reagents have been used widely only after the classic researches of L. A. Chugaev, who gave prominence to the study of the analytical properties of internally complex salts and proposed his well-known reaction for Ni^{++} with dimethylglyoxime (1905). This is still the best reaction for the Ni^{++} cation. The work of L. A. Chugaev started a new era in the development of analytical chemistry, characterized by extensive use of various organic compounds as reagents.

Since then a vast number of valuable organic reagents for various ions have been discovered; in conjunction with masking agents these are used to a particularly great extent in drop analysis. The search for organic reagents is one of the most important and fruitful directions of research in the field of qualitative analysis at the present time. Organic reagents are also of great importance in quantitative analysis. Many scientists are conducting researches into the theory of action and the practical applications of organic reagents in analysis.

In discussing the significance of complex compounds in analysis it is also necessary to note the influence of complex formation on the acid-base and oxidation-reduction properties of the compounds forming complexes.

If the anion of a weak acid is bound to a complex, its bond with H^+ ions is weakened and the resultant acid is stronger than the original one. For example, oxalic acid $H_2C_2O_4$ forms a considerably stronger acid in the presence of Mg^{++} ions which form a complex with $C_2O_4^{--}$ anions. The acidic properties of boric acid H_3BO_3 are also intensified in the presence of glycerol or glucose, etc.

If a fluoride is added to a solution of an aluminium salt, the stable complex $[AlF_6]^{---}$ is formed and the tendency of the Al^{+++} cation to combine with OH^- ions is diminished. Accordingly, the degree of hydrolysis of the aluminium salt is decreased. Many similar examples could be cited.

The oxidation-reduction properties of compounds are also altered by complex formation. The chemical activity of an oxidizing (or reducing) agent is usually diminished because its concentration in solution is decreased. For example, the Fe^{+++} ion becomes incapable of oxidizing I^- ions to I_2 when a fluoride is added, because it is bound in the stable complex $[FeF_6]^{---}$. Analogously, the reducing activity of oxalic acid is greatly diminished in the presence of excess molybdic acid, H_2MoO_4, which forms the complex $[H_2C_2O_4 \cdot MoO_3]$ with oxalic acid; as a result, $H_2C_2O_4$ is no longer oxidized by permanganate.

In some cases, however, the oxidizing activity of compounds is increased as the result of complex formation; this can sometimes be used for analytical purposes.

For example, Mo^{VI}, which is contained in molybdic acid and normal molybdates, cannot oxidize the organic reagent benzidine, $H_2N—C_6H_4—C_6H_4—NH_2$; but when it is in the complex phosphomolybdic acid $H_7[P(Mo_2O_7)_6]$ this oxidation occurs readily. This reaction is used for detection of the phosphate ion (PO_4^{---}).

Finally, it will be remembered (see Sec. 28) that complex formation can also be used for bringing certain sparingly soluble compounds into solution.

50. Oxidation-Reduction Reactions

Oxidation was originally understood to be the addition of oxygen or removal of hydrogen from a substance, while the reverse processes were termed reduction. However, further studies have shown that there are numerous reactions which do not involve either oxygen or hydrogen but are nevertheless oxidation-reduction processes. The concepts of "oxidation" and "reduction" therefore became vague and indefinite. They have acquired definite meaning only in the light of the modern electronic theory of the structure of matter. The first to apply the electronic theory to chemical phenomena was the eminent scientist L. V. Pisarzhevsky, who formulated the modern views on oxidation-reduction processes in 1913.

By the electronic theory, *all chemical processes involving the transfer of electrons between atoms or ions are oxidation-reduction reactions.* An example is the reaction

$$Sn^{++} + 2Fe^{+++} = Sn^{++++} + 2Fe^{++}$$

The essential changes in this reaction are that the Sn^{++} ion loses two electrons and becomes an Sn^{++++} ion; this can be schematically represented by the equation

$$Sn^{++} - 2e = Sn^{++++} \quad (1)$$

The electrons lost by the Sn^{++} ion are transferred to two Fe^{+++} ions, decreasing their charge:

$$2Fe^{+++} + 2e = 2Fe^{++} \quad (2)$$

It can be demonstrated experimentally that electron transfer does in fact occur in this reaction. Put 0.1 *M* solutions of $FeCl_3$

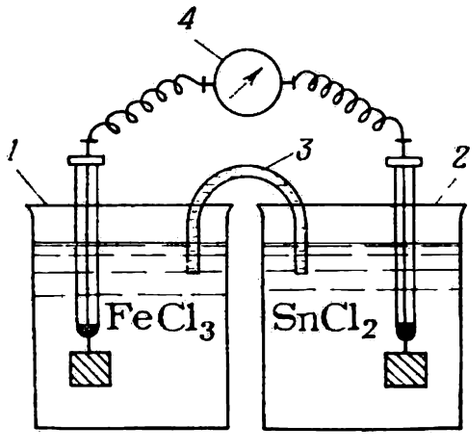


Fig. 28. Galvanic cell
1, *2*—beakers; *3*—electrolytic bridge; *4*—voltmeter

and $SnCl_2$, acidified with HCl to raise the conductivity, into separate beakers (*1* and *2* in Fig. 28) and join them by means of an "electrolytic bridge", i.e., a U-shaped tube *3* filled with KCl solution through which the ions can diffuse from one beaker into the other. Now immerse a platinum electrode into each solution and connect them by a conductor with a sensitive voltmeter *4* in the circuit. A deviation of the voltmeter needle shows that an electric current flows in the external circuit of our galvanic cell, and indicates its direction. In the present instance electrons travel from the $SnCl_2$ solution in beaker *2* to the $FeCl_3$ solution in beaker *1*. If after a while these solutions are tested with suitable reagents, it is found that Sn^{++++} ions have appeared in the $SnCl_2$ solution and Fe^{++} ions in the $FeCl_3$ solution.

This shows that the processes represented above by the Equations (1) and (2) occur in beakers *2* and *1* and that electrons are transferred from Sn^{++} ions to Fe^{+++} ions. Adding the two equations, we obtain the overall equation for the reaction taking place in the cell:

$$Sn^{++} + 2Fe^{+++} = Sn^{++++} + 2Fe^{++}$$

The Cl^- ions remain unchanged during the action of the cell, but are merely transferred from beaker *1* to beaker *2* through the tube *3*, carrying the current in the internal circuit.

An electric current may be produced by other oxidation-reduction reactions if they are conducted in galvanic cells.

Every such cell has a definite electromotive force (emf), which is a measure of the tendency of the reacting substances to redistribute electrons, and is therefore of great interest from the chemical standpoint. We will return to a study of emf later (Sec. 61).

As oxygen is a typical non-metal, its atoms tend to gain electrons. Therefore a substance which combines with oxygen (i.e., which is oxidized) gives electrons to it. Accordingly, *any chemical process in which atoms or ions lose electrons is regarded as oxidation. Conversely, reduction is a process which is the reverse of oxidation and is characterized by gain of electrons.*

For example, in the reaction discussed above Sn^{++} ions are oxidized to Sn^{++++} and Fe^{+++} ions are reduced to Fe^{++}.

More examples of oxidation-reduction processes are given below.*

$$2Cu + O_2 = 2CuO \quad (4e)$$

$$Cu + Cl_2 = CuCl_2 \quad (2e)$$

$$2I^- + Cl_2 = I_2 + 2Cl^- \quad (2e)$$

Loss of electrons by an atom or ion undergoing oxidation results in an increase of positive or a decrease of negative charge.** In the above examples Cu is oxidized to give Cu^{++} ions, Sn^{++} ions are oxidized to Sn^{++++}, I^- ions are converted into electrically neutral I_2, etc. However, the charge of an ion is equal to its valency, which is taken as positive for positively charged ions and negative for negative ions. This means that oxidation must increase the positive or decrease the negative valency of an element. Since a negative

---

* The arrows indicate electron transfer in the reactions.

** It must be understood that this refers to the charges of simple (elemental) ions of the reacting substances. The charge of an ion other than of this type may remain unchanged as the result of oxidation. For example, the charges of SO_3^{--} and SO_4^{--} ions are equal although the latter is the oxidation product of the former. Only if we consider the charges of the sulphur, which are $+4$ and $+6$ respectively in SO_3^{--} and SO_4^{--} ions, do we see that here too the charge is increased on oxidation.

quantity is regarded as larger if its absolute magnitude is smaller, we can say that *valency always increases as the result of oxidation.*

In the above examples the valencies of copper in CuO (+2), of tin in Sn^{++++} (+4) and of free I_2 (0) are greater than those of metallic copper (0), Sn^{++} ions (+2) and I^- ions (—1).

In contrast, *reduction, which is the reverse of oxidation, results in decrease of valency and increase of negative or decrease of positive charges of ions.*

The electrons in these reactions do not remain free, but merely pass from atoms or ions to others; therefore the oxidation of one substance is always accompanied by the reduction of another. Either of the processes in isolation is inconceivable.

A substance which causes oxidation of some other substance, and is itself reduced in the process, is known as an *oxidizing agent.* Conversely, a substance which is oxidized in a reaction and thereby reduces another substance is a *reducing agent.*

From all this it is clear that *the function of an oxidizing agent in a reaction is to gain electrons from the substance oxidized. The reducing agent, i.e., the substance oxidized, loses electrons.*

Since the electrons do not remain free, *the number of electrons given up by the reducing agent must be equal to the number gained by the oxidizing agent.* This fact may be used for calculating the coefficients in equations of oxidation-reduction reactions. The number of electrons lost or gained is deduced from the change in the valencies of the corresponding elements in the reaction. The valency can usually be established from the following considerations.

(1) The valencies of hydrogen and the metals are nearly always positive, and the valency of hydrogen is +1.

(2) Oxygen is usually negatively bivalent (with some very rare exceptions).

(3) The valencies of the remaining elements may be either positive or negative.

(4) The sum of the valencies of the atoms (or ions) constituting a molecule is zero. The valencies of atoms of free elements are taken as zero.

As an example, let us find the valency of nitrogen in HNO_3:

Valency of 1 hydrogen atom	+1
Valency of 3 oxygen atoms	—6
Leaving for 1 nitrogen atom	+5
Total . .	0

The valency of Cr in $K_2Cr_2O_7$ is +6 (2K = +2, 7O = —14, 2Cr = +12); the valency of Mn in the MnO_4^- ion is +7 (4O= —8, the sum of the valencies is —7, which leaves +7 for Mn), etc.

In the light of this, let us derive the equation for the oxidation of $FeSO_4$ by HNO_3 in the presence of H_2SO_4. We first write the formulas of all the substances taken and formed in the reaction:

$$FeSO_4 + HNO_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + NO + H_2O$$

Next we find the coefficients. Since the valency of Fe is +2 in $FeSO_4$ and +3 in $Fe_2(SO_4)_3$, the iron ion loses one electron in the reaction. At the same time the valency of the nitrogen atom (ion) changes from +5 (in HNO_3) to +2 (in NO). Therefore the redistribution of electrons taking place in the reaction can be represented as follows*:

$$\begin{array}{r|l} 2Fe^{++} - 2e = 2Fe^{+++} & 3 \\ N^{+V} + 3e = N^{+II} & 2 \end{array}$$

The coefficient of Fe^{++} is taken as 2 because there cannot be less than two iron ions in the molecular equation for the reaction; otherwise a fractional number of $Fe_2(SO_4)_3$ molecules would be obtained.

To equate the numbers of electrons lost and gained we must multiply the first of the above equations by 3 and the second by 2, as indicated by the numbers on the right of the line. In other words, six $FeSO_4$ molecules and two HNO_3 molecules must take part in the reaction:

$$6FeSO_4 + 2HNO_3 + H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + H_2O$$

We now find the coefficients of H_2SO_4 and H_2O. The three molecules of $Fe_2(SO_4)_3$ formed in the reaction contain $9SO_4^{--}$ anions, whereas in the six $FeSO_4$ molecules taken there are only 6. Therefore three H_2SO_4 molecules must take part in the reaction. Since these molecules contain 6 hydrogen ions and there are 2 hydrogen ions in two HNO_3 molecules, 4 water molecules are formed. The required equation is therefore

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO\uparrow + 4H_2O$$

To verify it, we count the numbers of oxygen atoms (ions) in each side:

Left-hand side . . . . . $6\times4+2\times3+3\times4=42$
Right-hand side . . . . $3\times12+2+4=42$

The equation balances.

We now write it in ionic form:

$$6Fe^{++} + 6SO_4^{--} + 2H^+ + 2NO_3^- + 6H^+ + 3SO_4^{--} =$$
$$= 6Fe^{+++} + 9SO_4^{--} + 2NO + 4H_2O$$
$$6Fe^{++} + 8H^+ + 2NO_3^- = 6Fe^{+++} + 2NO\uparrow + 4H_2O$$

---

* The valencies of elements contained in composite ions or molecules are denoted by Roman numerals (with plus or minus signs if necessary).

and finally

$$3Fe^{++} + 4H^+ + NO_3^- = 3Fe^{+++} + NO\uparrow + 2H_2O$$

We will now derive the equation for oxidation of $Mn(NO_3)_2$ to $HMnO_4$ by lead dioxide in the presence of nitric acid:

$$Mn(NO_3)_2 + PbO_2 + HNO_3 \longrightarrow HMnO_4 + Pb(NO_3)_2 + H_2O$$

$$\begin{array}{r|l} Mn^{++} - 5e = Mn^{+VII} & 2 \\ Pb^{+IV} + 2e = Pb^{++} & 5 \end{array}$$

$$2Mn(NO_3)_2 + 5PbO_2 + HNO_3 \longrightarrow 2HMnO_4 + 5Pb(NO_3)_2 + H_2O$$

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O$$

Left-hand side . . . . . 12+10+18=40 oxygen atoms (ions)
Right-hand side . . . . 8+30+2=40 oxygen atoms (ions)

The equation balances.

The ionic equation of the reaction is

$$2Mn^{++} + 5PbO_2 + 4H^+ = 2MnO_4^- + 5Pb^{++} + 2H_2O$$

Several more examples of writing the equations for oxidation-reduction reactions are given below.

(1) $$K_2Cr_2O_7 + KI + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + I_2 + H_2O$$

$$\begin{array}{r|l} 2I^- - 2e = I_2 & 3 \\ 2Cr^{+VI} + 6e = 2Cr^{+++} & 1 \end{array}$$

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

(2) $$KMnO_4 + H_2S + HCl \longrightarrow MnCl_2 + KCl + S + H_2O$$

$$\begin{array}{r|l} S^{--} - 2e = S & 5 \\ Mn^{+VII} + 5e = Mn^{++} & 2 \end{array}$$

$$2KMnO_4 + 5H_2S + 6HCl = 2MnCl_2 + 2KCl + \downarrow 5S + 8H_2O$$

(3) $$CoS + HNO_3 \longrightarrow Co(NO_3)_2 + S + NO + H_2O$$

$$\begin{array}{r|l} S^{--} - 2e = S & 3 \\ N^{+V} + 3e = N^{+II} & 2* \end{array}$$

$$3CoS + 8HNO_3 = 3Co(NO_3)_2 + 3S + 2NO\uparrow + 4H_2O$$

(4) $$Mn(NO_3)_2 + NaBiO_3 + HNO_3 \longrightarrow HMnO_4 + Bi(NO_3)_3 + NaNO_3 + H_2O$$

$$\begin{array}{r|l} Mn^{++} - 5e = Mn^{+VII} & 2 \\ Bi^{+V} + 2e = Bi^{+++} & 5 \end{array}$$

$$2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 = 2HMnO_4 + 5Bi(NO_3)_3 + 5NaNO_3 + 7H_2O$$

---

* The coefficient 2 taken for HNO_3 must be increased to 8, because 6 more molecules of HNO_3 are required to form 3 molecules of $Co(NO_3)_2$.

(5) $$MnO(OH)_2 + Na_2CO_3 + KClO_3 \longrightarrow Na_2MnO_4 + KCl + H_2O + CO_2$$

$$\begin{array}{r|l} Mn^{+IV} - 2e = Mn^{+VI} & 3 \\ Cl^{+V} + 6e = Cl^- & 1 \end{array}$$

$$3MnO(OH)_2 + 3Na_2CO_3 + KClO_3 = 3Na_2MnO_4 + KCl + 3H_2O + 3CO_2 \uparrow$$

(6) $$As_2S_3 + HNO_3 + H_2O \longrightarrow H_3AsO_4 + H_2SO_4 + NO$$

When deriving this equation bear in mind that the As_2S_3 molecule loses a total of 28 electrons, because

$$2As^{+III} - 2 \cdot 2e = As^{+V}$$

$$3S^{-II} - 3 \cdot 8e = 3S^{+VI}$$

Therefore we have

$$\begin{array}{r|l} As_2S_3 - 28e = 2As^{+V} + 3S^{+VI} & 3 \\ N^{+V} + 3e = N^{+II} & 28 \end{array}$$

$$3As_2S_3 + 28HNO_3 + 4H_2O = 6H_3AsO_4 + 9H_2SO_4 + 28NO \uparrow$$

It must be pointed out that difficulties sometimes arise in this method of finding the coefficients in the equations of oxidation-reduction reactions. Consider, for example, the oxidation of chromium (III) to CrO_4^{--} ions by hydrogen peroxide in alkaline solution. In alkaline solution chromium (III) is present as chromite, such as $KCrO_2$. We can therefore write

$$KCrO_2 + H_2O_2 + KOH \longrightarrow K_2CrO_4 + H_2O$$

In this reaction electrons are given up by Cr^{+III} (which is converted into Cr^{+VI}) while they are gained evidently by H_2O_2, which is the oxidizing agent in this reaction. Since the valency of hydrogen, with only one electron in its atom, cannot be greater than +1, the valency of oxygen in H_2O_2 must be taken as —1. At the same time, the structural formula of hydrogen peroxide

$$H—O—O—H$$

shows that oxygen is bivalent here too, but some of the valency units are used for joining oxygen atoms together. Evidently in the calculation we took into account only the oxygen valencies used for satisfying the valencies of the hydrogen atoms, and so we obtained a fictitious valency for oxygen. All these difficulties are easily avoided if it is noted that H_2O_2, which is a weak acid, must yield O_2^{--} anions by dissociation. In the reaction each such anion changes into two O^{--} ions which are used in the formation of H_2O molecules and CrO_4^{--} anions. Two O^{--} ions contain a total of 4 excess electrons. Therefore the redistribution of electrons may be schematically represented as follows:

$$\begin{array}{r|l} Cr^{+III} - 3e = Cr^{+VI} & 2 \\ O_2^{--} + 2e = 2O^{--} & 3 \end{array}$$

From this we find the equation for the reaction:

$$2KCrO_2 + 3H_2O_2 + 2KOH = 2K_2CrO_4 + 4H_2O$$

or

$$2CrO_2^- + 3H_2O_2 + 2OH^- = 2CrO_4^{--} + 4H_2O$$

Similar difficulties will be encountered in the case of oxidation by ammonium persulphate, $(NH_4)_2S_2O_8$, and reduction by oxalic acid, $H_2C_2O_4$. The derivation of the corresponding equations will be discussed later.

All these difficulties and inconveniences can be avoided by using the so-called *electron-ion* method for deriving the equations for oxidation-reduction reactions. It was pointed out above (p. 242) that any oxidation-reduction process can serve as a source of electric current if it takes place in a galvanic cell. For this the oxidizing and reducing agents must be separated from each other, i.e., be in different vessels, but capable of electron transfer. The reducing agent is oxidized in one vessel, and the oxidizing agent (which receives the electrons lost by the reducing agent through the metallic conductor) is reduced in the other. If we write separately the equations for the reactions in the two vessels, equate the numbers of electrons lost and gained, and add the two equations, we obtain the overall equation for the oxidation-reduction process taking place during operation of the cell.

Consider the following examples.

1. First, we derive the ionic equation for the oxidation of I^- ions by Fe^{+++} ions. The oxidation of I^- ions to I_2, in one of the vessels of the cell, corresponds to the equation

$$2I^- - 2e = I_2$$

In the other vessel Fe^{+++} ions gain electrons and are reduced to Fe^{++}:

$$Fe^{+++} + e = Fe^{++}$$

To balance the numbers of electrons lost and gained we multiply the second equation by 2 and then add the two equations:

$$\begin{gathered} 2I^- - 2e = I_2 \\ 2Fe^{+++} + 2e = 2Fe^{++} \\ \hline 2I^- + 2Fe^{+++} = I_2 + 2Fe^{++} \end{gathered}$$

This is the ionic equation for oxidation of the I^- ion.

2. Let us examine the oxidation of $C_2O_4^{--}$ ions by MnO_4^- ions in acid solution. Here the reducing agent is $C_2O_4^{--}$ which is itself oxidized to CO_2. This reaction may be represented by the equation

$$C_2O_4^{--} - 2e = 2CO_2 \qquad (1)$$

The oxidizing agent (the MnO_4^- ion) gains electrons and is reduced to Mn^{++}:

$$MnO_4^- + H^+ + e \longrightarrow Mn^{++} + H_2O$$

However, this expression is incorrect, firstly because the numbers of H and O atoms are not the same on both sides. To balance the equation we note that the oxygen of the MnO_4^- ion combines with hydrogen ions to give H_2O molecules. Eight H^+ ions are needed to combine with four O atoms, and four molecules of H_2O are formed. We can therefore write

$$MnO_4^- + 8H^+ + e \longrightarrow Mn^{++} + 4H_2O$$

Now the numbers of the atoms balance. However, the expression is still wrong because the charges are different on the two sides. The sum of the ionic charges in the left-hand side is $-1 + 8 - 1 = +6$, whereas in the right-hand side it is only $+2$. To balance the charges we must evidently take 5 electrons and not one in the left-hand side, because $-1 + 8 - 5 = +2$. Therefore the reduction of the oxidizing agent (MnO_4^- ions) to Mn^{++} cations can be represented as follows:

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O \qquad (2)$$

To balance the numbers of electrons given up by the $C_2O_4^{--}$ ions and gained by the MnO_4^- ions we multiply Equation (1) by 5 and Equation (2) by 2, and then add the two equations:

$$5C_2O_4^{--} - 10e = 10CO_2$$

$$2MnO_4^- + 16H^+ + 10e = 2Mn^{++} + 8H_2O$$

$$5C_2O_4^{--} + 2MnO_4^- + 16H^+ = 2Mn^{++} + 10CO_2\uparrow + 8H_2O$$

As a check, we count the oxygen atoms and charges in both sides of this ionic equation:

Charges	$-10-2+16=+4$
Oxygen atoms . .	$20+8=20+8$

The equation is correct.

This example shows that *with this method of deriving the reaction equations it is not necessary to know the valencies of the elements.* because a purely arithmetical operation of counting and balancing the total charges in the two partial Equations (1) and (2) is all that is needed to find the numbers of electrons gained and lost. If the equation had been derived by the valency change method, we would have obtained an erroneous valency for carbon ($+3$), as carbon is quadrivalent in this case too.

Another advantage of the electron-ion method is that we deal with ions which actually exist in the solution, such as MnO_4^- or CrO_4^{--}. and not with hypothetical ions such as Mn^{+VII} or Cr^{+VI}.

3. Let us derive the equation for oxidation of Cr^{+++} to $Cr_2O_7^{--}$ by the persulphate ion, $S_2O_8^{--}$. For the reducing agent we can write

$$2Cr^{+++} \longrightarrow Cr_2O_7^{--}$$

It might seem that the missing oxygen atoms must come from the oxidizing agent, i.e., $S_2O_8^{--}$ ions. However, it must be remembered that in this method we consider the reaction to occur in a cell, where the Cr^{+++} and $S_2O_8^{--}$ ions are in different vessels. This means that only water can be the source of oxygen. Therefore the partial equation for the reducing agent is*

$$2Cr^{+++} + 7H_2O - 6e = Cr_2O_7^{--} + 14H^+$$

For the oxidizing agent, $S_2O_8^{--}$, we write

$$S_2O_8^{--} + 2e = 2SO_4^{--}$$

Hence

$$\begin{gathered} 2Cr^{+++} + 7H_2O - 6e = Cr_2O_7^{--} + 14H^+ \\ 3S_2O_8^{--} + 6e = 6SO_4^{--} \\ \hline 2Cr^{+++} + 3S_2O_8^{--} + 7H_2O = Cr_2O_7^{--} + 6SO_4^{--} + 14H^+ \end{gathered}$$

The charge balance: $+6 - 6 = -2 - 12 + 14$ shows that the equation is correct.

4. We now derive the equation for oxidation of CrO_2^- ions to CrO_4^{--} by H_2O_2 in alkaline solution. For the reducing agent, CrO_2^- ions, we have

$$CrO_2^- \longrightarrow CrO_4^{--}$$

For the reason explained above the lacking two oxygen atoms are taken from two H_2O molecules:

$$CrO_2^- + 2H_2O \longrightarrow CrO_4^{--} + 4H^+$$

The sum of the ionic charges is -1 on the left-hand side and $+2$ on the right. The CrO_2^- ion, being the reducing agent, loses electrons in the reaction, and the loss of one electron is equivalent to the gain of one positive charge. To balance the numbers of electrons on both sides, the charge in the left-hand side of the equation must be increased by $+3$, that is, three electrons must be removed, and then

$$CrO_2^- + 2H_2O - 3e = CrO_4^{--} + 4H^+$$

For the oxidizing agent, H_2O_2, we write

$$H_2O_2 + 2e = 2OH^-$$

---

* In this equation the charge balance is

$$+6 - (-6) = -2 + 14$$

The loss of one electron is equivalent to an increase of the charge by one unit.

Hence

$$2CrO_2^- + 4H_2O - 6e = 2CrO_4^{--} + 8H^+$$
$$3H_2O_2 + 6e = 6OH^-$$
$$8H^+ + 8OH^- = 8H_2O$$
$$\overline{2CrO_2^- + 3H_2O_2 + 2OH^- = 2CrO_4^{--} + 4H_2O}$$

We must write the third equation because the reaction occurs in alkaline solution and the H^+ ions formed do not remain free but combine with the OH^- ions of the alkali.

The same equation is obtained if OH^- ions are taken as the source of oxygen in the conversion of CrO_2^- ions into CrO_4^{--}. However, the correct equation here is

$$CrO_2^- + 4OH^- - 3e = CrO_4^{--} + 2H_2O$$

and not

$$CrO_2^- + 2OH^- - 2e = CrO_4^{--} + 2H^+$$

because H^+ ions cannot be obtained by the action of OH^- ions.

5. In the above example the oxidizing agent was H_2O_2. However, hydrogen peroxide acts as a reducing agent towards the strongest oxidizing agents, such as $KMnO_4$, $K_2Cr_2O_7$, $MnO(OH)_2$, and is itself oxidized to free O_2:

$$H_2O_2 - 2e = O_2\uparrow + 2H^+$$

As an example, we derive the equation for reduction of MnO_4^- to Mn^{++} by H_2O_2 in acid solution:

$$5H_2O_2 - 10e = 5O_2 + 10H^+$$
$$2MnO_4^- + 16H^+ + 10e = 2Mn^{++} + 8H_2O$$
$$\overline{2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{++} + 5O_2\uparrow + 8H_2O}$$

6. Oxidation of hydrogen sulphide by MnO_4^- ions in acid solution:

$$5H_2S - 10e = 5S + 10H^+$$
$$2MnO_4^- + 16H^+ + 10e = 2Mn^{++} + 4H_2O$$
$$\overline{5H_2S + 2MnO_4^- + 6H^+ = 2Mn^{++} + \downarrow 5S + 4H_2O}$$

7. Oxidation of I^- ions by $Cr_2O_7^{--}$ in acid solution:

$$6I^- - 6e = 3I_2$$
$$Cr_2O_7^{--} + 14H^+ + 6e = 2Cr^{+++} + 7H_2O$$
$$\overline{6I^- + Cr_2O_7^{--} + 14H^+ = 3I_2 + 2Cr^{+++} + 7H_2O}$$

8. Dissolution of FeS in HNO_3:

$$FeS - 3e = Fe^{+++} + S$$
$$NO_3^- + 4H^+ + 3e = NO + 2H_2O$$
$$FeS + NO_3^- + 4H^+ = Fe^{+++} + \downarrow S + NO \uparrow + 2H_2O$$

9. Oxidation of Mn^{++} ions to MnO_4^- by the action of $NaBiO_3$:

$$2Mn^{++} + 8H_2O - 10e = 2MnO_4^- + 16H^+$$
$$5NaBiO_3 + 30H^+ + 10e = 5Na^+ + 5Bi^{+++} + 15H_2O$$
$$2Mn^{++} + 5NaBiO_3 + 14H^+ = 2MnO_4^- + 5Na^+ + 5Bi^{+++} + 7H_2O$$

10. Oxidation of Mn^{++} ions to MnO_4^- by $S_2O_8^{--}$ ions:

$$2Mn^{++} + 8H_2O - 10e = 2MnO_4^- + 16H^+$$
$$5S_2O_8^{--} + 10e = 10SO_4^{--}$$
$$2Mn^{++} + 5S_2O_8^{--} + 8H_2O = 2MnO_4^- + 10SO_4^{--} + 16H^+$$

QUESTIONS AND PROBLEMS

1. What are the differences between double and complex salts?
2. One characteristic test for Fe^{+++} is the action of ammonium thiocyanate, NH_4CNS, with formation of ferrithiocyanate,* $Fe(CNS)_3$, which imparts a blood-red colour to the solution. Explain why this colour is produced with $(NH_4)Fe(SO_4)_2$ and not with $K_3[Fe(CN)_6]$.
3. The reaction of $K_3[Fe(CN)_6]$ with Fe^{II} salts is represented by the equation

$$2K_3[Fe(CN)_6] + 3FeSO_4 = Fe_3[Fe(CN)_6]_2 + 3K_2SO_4$$

Write the ionic equation for this reaction.

4. Give (a) the charges of the complex ions; (b) the coordination numbers and charges of the complex-formers in the following compounds: $K_2[PtCl_6]$; $H[AuCl_4]$; $[Co(NH_3)_6]SO_4$; $Na_3[Co(NO_2)_6]$.
5. Indicate the variations of (a) the charges of the complexes and (b) the composition of the outer coordination sphere in the following series of compounds: $[Co(NH_3)_6]Cl_3$; $[Co(NH_3)_5NO_2]Cl_2$; $[Co(NH_3)_3(NO_2)_3]$; $[Co(NO_2)_6]K_3$.
How should the conductivities of solutions of the same molar concentrations vary in this series of compounds?
6. Two compounds, both having the empirical formula $PtCl_2Br_2 \cdot 4NH_3$, react differently with $AgNO_3$ solution. One gives a precipitate of AgCl and the other of AgBr, with $AgNO_3$. Explain the difference and write the coordination formula of each compound.
7. Name the reagents which could be used to distinguish between two isomers both having the empirical formula $CoBrSO_4 \cdot 5NH_3$.
8. Explain how the dissociation of complexes influences the course of precipitation reactions.
9. State the factors determining whether precipitates are formed with various complex silver salts by the action of reagents which precipitate Ag^+ ions.

---

* And also various iron thiocyanate complexes (see p. 227).

10. Calculate the concentrations of Ag^+ ions in 0.1 *M* solutions of the following complex salts: $[Ag(NH_3)_2]NO_3$; $Na[AgS_2O_3]$; $K[Ag(CN)_2]$.

Answer. 5.5×10^{-3} *M*; 1×10^{-7} *M*; 2.9×10^{-8} *M*.

11. Using the answers to the previous problem find whether $AgBrO_3$ ($SP = 5.8 \times 10^{-5}$) and AgI are precipitated from 0.2 *M* $Na[AgS_2O_3]$ solution by equal volumes of (a) 0.2 *M* $KBrO_3$; (b) 0.2 *M* KI.

12. The complex salt $K[Ag(CN)_2]$ is prepared by the action of *excess* KCN on $AgNO_3$. Find the excess concentration of KCN which is needed to prevent precipitation of AgI when equal volumes of 0.2 *M* solutions of $K[Ag(CN)_2]$ and KI are mixed.

Answer. 2.6×10^{-4} *M* or higher.

13. Treatment of the complex cadmium ammine $[Cd(NH_3)_4]SO_4$ in solution with KCN gives a complex cadmium cyanide. Write the molecular and ionic equations for this reaction and explain why it occurs.

14. The Cd^{++} ion gives a white precipitate of $Cd(OH)_2$ with alkalies and a yellow precipitate of CdS with H_2S. However, if an excess of KCN is added to a solution of a cadmium salt before treatment with these reagents, only H_2S gives a precipitate while alkalies do not. Explain this.

15. Explain why a large amount of Ag_2S is precipitated by the action of H_2S on a solution of $K[Ag(CN)_2]$ despite the low concentration of Ag^+ ions.

16. Explain how Fe^{+++} ions may be masked when they interfere with the detection of other ions. Give other examples of the masking of interfering ions in analysis.

17. For quantitative determination of nickel in steel a weighed sample of the steel is dissolved in HCl, Fe^{++} is oxidized to Fe^{+++} by nitric acid, and tartaric (or citric) acid is added to the solution. The solution is then made alkaline with ammonia and Ni^{++} is precipitated by dimethylglyoxime (p. 237). The precipitate is filtered off, washed, and dried at 120° (or ignited). The amount of nickel present in the steel sample is found from the weight and formula of the precipitate. Explain the purpose of adding tartaric (or citric) acid in the precipitation of nickel.

18. What are internally complex salts? Write the structural formulas of copper aminoacetate and nickel dimethylglyoximate.

19. Explain why the formation of internally complex salts is of great significance in analysis.

20. Discuss the potentialities of searches of organic reagents for various ions for analytical chemistry.

21. Write the ionic equations for the following reactions and indicate which ions or atoms are oxidized and reduced:

$$CuSO_4 + Fe = FeSO_4 + \downarrow Cu$$

$$Ag_2SO_4 + 2FeSO_4 = \downarrow 2Ag + Fe_2(SO_4)_3$$

$$2KI + Br_2 = 2KBr + I_2$$

$$SnCl_2 + 2HgCl_2 = \downarrow Hg_2Cl_2 + SnCl_4$$

What are the valency changes of the oxidized and reduced atoms in these reactions?

22. Find the coefficients in the following oxidation-reduction reactions and indicate which substances are the oxidizing or reducing agents:

$$FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + K_2SO_4 + MnSO_4 + H_2O$$

$$KMnO_4 + KNO_2 + H_2SO_4 \longrightarrow KNO_3 + K_2SO_4 + MnSO_4 + H_2O$$

$$H_2O_2 + KI + HCl \longrightarrow I_2 + KCl + H_2O$$

$$MnO(OH)_2 + H_2O_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + O_2\uparrow$$

$$KClO_3 + FeCl_2 + HCl \longrightarrow KCl + FeCl_3 + H_2O$$

$$Na_2SO_3 + Na_2Cr_2O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

$$Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + HI$$

$$CuS + HNO_3 \longrightarrow Cu(NO_3)_2 + NO\uparrow + H_2O + \downarrow S$$

$$As_2S_5 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO\uparrow + H_2O$$

$$K_2Cr_2O_7 + H_2SO_4 + H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + \downarrow S + H_2O$$

$$KMnO_4 + H_2SO_4 + H_2S \longrightarrow K_2SO_4 + MnSO_4 + \downarrow S + H_2O$$

$$KMnO_4 + KCrO_2 + H_2O \longrightarrow K_2CrO_4 + \downarrow MnO(OH)_2$$

23. Use the ion-electron method for writing the ionic equations of the following reactions:

$$Fe^{++} + NO_3^- + H^+ \longrightarrow Fe^{+++} + NO\uparrow + H_2O$$

$$Mn^{++} + PbO_2 + H^+ \longrightarrow MnO_4^- + Pb^{++} + H_2O$$

$$ClO_3^- + SO_3^{--} + H^+ \longrightarrow Cl^- + SO_4^{--} + H_2O$$

$$I^- + NO_2^- + H^+ \longrightarrow I_2 + NO\uparrow + H_2O$$

$$Cr^{+++} + S_2O_8^{--} + H_2O \longrightarrow Cr_2O_7^{--} + SO_4^{--} + H^+$$

REACTIONS AND ANALYTICAL PROCEDURE FOR GROUP III CATIONS

51. General Characteristics of Group III Cations

Group III contains the ions of aluminium, chromium, iron, manganese, zinc, cobalt, nickel, and certain other metals. *The cations of this group differ from Groups I and II by forming sulphides which are almost insoluble in water but dissolve in dilute acids or are decomposed by water to form hydroxides which are soluble in acids.*

As they are soluble in acids, Group III sulphides cannot be precipitated by H_2S in acid solution. In neutral solution Group III sulphides are either not precipitated at all, or the precipitation is incomplete (in the case of Zn^{++}).

This is because H_2S is *a very weak acid and gives such a low concentration of* S^{--} *ions in solution that the solubility products of most of the Group III sulphides cannot be reached. However, if instead of* H_2S *one of its soluble salts is used, such salts being highly dissociated, Group III cations are precipitated completely; for example:*

$$MnSO_4 + (NH_4)_2S = \downarrow MnS + (NH_4)_2SO_4$$

Therefore Group III cations are separated either by the action of H_2S at $pH \geqslant 7.2$ (for example, in the presence of ammonium buffer mixture of pH = 8-9) or *by the action of ammonium sulphide,* $(NH_4)_2S$, *which is the Group III group reagent.**

Under suitable conditions (see Sec. 52) the group reagent precipitates most of the Group III cations as the corresponding sulphides—Fe_2S_3, FeS, MnS, NiS and CoS. The exceptions are Al^{+++} and Cr^{+++}; the corresponding hydroxides $Al(OH)_3$ and $Cr(OH)_3$ are less soluble than the sulphides, and are therefore precipitated by $(NH_4)_2S$. Apart from Al^{+++} and Cr^{+++}, many other Group III cations not considered in this book are precipitated as the hydroxides (Be^{++}, Sc^{+++}, La^{+++}, Zr^{++++}, and others).

The analytical Group III cations which are precipitated as the sulphides are in the middle of the fourth long period of the Mendeleyev periodic system, i.e., where the third electron shell is built up from 8 to 18 electrons. Therefore these cations usually have incomplete

---

* A detailed theoretical discussion of all these facts, important in analysis, is given in Sections 39 and 40.

outer electron shells (see Table 3 on p. 34). The exception is Zn^{++}, which has a complete 18-electron shell, but in its properties (precipitation by hydrogen sulphide) it is intermediate between the cations of analytical Groups III and IV.

Apart from Cr^{+++} and Be^{++}, the Group III cations precipitated by the group reagent as the hydroxides are in Groups III-V of the periodic system in the short periods or in the first half of a long period. Like the cations of the first two groups, they have complete external shells of 8 electrons (with the exception of Cr^{+++}).

Several characteristics of importance in analysis, which distinguish this group from analytical Groups I and II, are associated with the positions of the elements forming the Group III cations in the Mendeleyev periodic system.

1. Ion Valencies. In the analytical groups studied previously we were concerned with cations of elements of Groups I and II of the periodic system. Each such element forms only one salt-forming oxide and is therefore always present in solution in the form of ions of one valency only. In contrast to this, the cations of analytical Group III include elements belonging to very diverse groups (II, III, VI, VII and VIII) of the periodic system.* Only the elements of the lowest groups (II and III), zinc and aluminium, giving the cations Zn^{++} and Al^{+++}, have constant valencies. The elements of the higher groups of the periodic system, namely chromium (Group VI), manganese (Group VII), and iron, cobalt and nickel (Group VIII), exist in several states of oxidation and can therefore be present in solutions as ions of different valencies. For example, all these elements (except nickel and cobalt)** form bivalent cations (salts of the lower oxide) and trivalent cations (salts of the higher oxide). Of course, ions of different valencies differ in their reactions. However, not all these ions are stable. The Mn^{+++} and Cr^{++} ions are extremely unstable and are readily converted into Mn^{++} and Cr^{+++} under analytical conditions. Therefore we will not consider them here. On the other hand, both the iron cations, Fe^{++} and Fe^{+++}, are fairly stable. We will therefore study the following cations: Al^{+++}, Cr^{+++}, Fe^{+++}, Fe^{++}, Mn^{++}, Zn^{++}, Co^{++} and Ni^{++}.

2. Chemical Character of the Oxides and Hydroxides. Analytical Groups I and II include the alkali and alkaline earth metals, which are the elements with the most pronounced metallic properties.

---

* If the Group III cations not considered in this book are also taken into account, it will be found that the group includes elements from all the groups of the periodic system except the first and zero groups.

** Cobalt (III) can exist in solutions only in the form of complex ions. Nickel (III) forms only the oxide Ni_2O_3 and the corresponding hydroxide $Ni(OH)_3$.

For example, their hydroxides (with the exception of magnesium hydroxide) are among the strongest and most soluble bases.

However, as we pass further to the right in the periodic system the metallic properties of the elements become weaker and the non-metallic characteristics stronger, reaching a maximum in Group VII in the second half of the long periods. Accordingly, the hydroxides of the elements in analytical Group III are either weak bases, sparingly soluble in water, or are amphoteric, or may even be typical acids. In accordance with the general rule, acidic behaviour is most pronounced in elements of Groups VI and VII of the periodic system in the highest oxidation states. For example, chromium, a Group VI element, forms the oxides CrO, Cr_2O_3 and CrO_3. The first of these, chromous oxide CrO, is a basic oxide. It corresponds to the hydroxide $Cr(OH)_2$, which is a weak base forming salts with acids only. The oxide Cr_2O_3, chromic oxide, is amphoteric, because it forms salts with both acids and bases, for example, $CrCl_3$, $KCrO_2$. The oxide CrO_3 is acidic (chromic anhydride), corresponding to chromic acid H_2CrO_4 and dichromic acid $H_2Cr_2O_7$. Therefore trivalent chromium may exist in solution either as Cr^{+++} cations or as CrO_2^- anions; the former predominate in acid and the latter in alkaline solutions (see Sec. 45). Chromium (VI) exists in solution only as CrO_4^{--} anions (alkaline solutions) or as $Cr_2O_7^{--}$ anions (acid solutions).

Similarly, manganese forms the oxides MnO, Mn_2O_3, MnO_2, MnO_3 and Mn_2O_7, of which the first two are basic and the last three acidic. The acidic oxides correspond to the acids $MnO(OH)_2$ or H_2MnO_3 (manganous), H_2MnO_4 (manganic), and $HMnO_4$ (permanganic). Of the ions formed by manganese, we will study the Mn^{++} cation and the MnO_4^- (permanganate) anion. Although the latter, like the CrO_4^{--} and $Cr_2O_7^{--}$ anions, are detected during analytical tests for anions, their most important reactions are considered here together with the reactions of the Mn^{++} and Cr^{+++} cations, with which they are closely associated.

The hydroxides of elements of Group VIII of the periodic system (iron, cobalt and nickel) are weak bases.

The hydroxides of aluminium and zinc are amphoteric; this property is used in analysis for separating them from most of the other Group III cations.

3. Hydrolysis of Salts. Since the basic properties of the Group III hydroxides are weak, the corresponding salts should undergo considerable hydrolysis. As the result of hydrolysis, *solutions of salts of strong acids have an acid reaction* (pH < 7). The pH of solutions of various salts can be approximately estimated from the data in Table 10 (p. 128), giving the pH at which precipitation of hydroxides from salt solutions begins; these values were calculated from the corresponding solubility products. For example, the precipitation

of $Fe(OH)_3$ from 0.01 *M* $FeCl_3$ solution begins at pH = 2.2; therefore the pH of this solution must be less than 2.2.

At higher concentrations solutions of ferric salts must be even more acidic. For example, the pH of 1 *M* $FeCl_3$ or $Fe_2(SO_4)_3$ cannot be higher than 1.5, the value at which precipitation of $Fe(OH)_3$ begins in this case. Aluminium and chromium (III) salts, like ferric salts, should also form fairly acidic solutions because precipitation of $Al(OH)_3$ from 0.01 *M* solutions of its salts begins at pH = 3.8, and that of $Cr(OH)_3$ at pH = 4.6. In contrast, solutions of cobalt, nickel, manganese and zinc salts should be only slightly acidic. Although the calculations on which these conclusions are based are crude approximations, with a few rare exceptions they are in good agreement with experimental results. For example, according to N. A. Tananaev's data, the pH of 0.01 *M* solutions of cobalt, nickel, manganese (II) and zinc is about 6, while at the same concentrations the pH of ferric salts is about 2, that of aluminium salts is 2-4, and that of chromium (III) salt is 2-3.

Acids are sometimes added to solutions of salts to suppress hydrolysis which might lead to precipitation of basic salts of hydroxides on keeping. For example, solutions of ferric and ferrous salts and $AlCl_3$ solutions are always acidified. Therefore the pH of such solutions is usually 1 or less.

Because of the sharp differences in pH of various salt solutions, the pH of an unknown solution may often be an important indication of the possible presence or absence of particular ions.

The hydrolysis of salts of very weak acids such as H_2S, H_2CO_3, HCN, etc., is sometimes so extensive (in the case of aluminium and chromic salts) that the salts cannot exist at all in aqueous solution. Therefore when a reagent acts on a solution containing ions which form such salts, the corresponding hydroxides are formed.

4. Oxidation-Reduction Properties. In our study of the cations of Groups I and II we were concerned entirely with exchange reactions. Oxidation-reduction (redox) reactions are not used in analysis of these groups because the elements of Groups I and II have constant valencies. Analytical Group III includes some elements of the higher groups of the periodic system, having variable valencies. Oxidation-reduction reactions are therefore widely used in analysis of Group III. They are especially important for detection and separation of manganese, chromium and iron.

It is evident that the ions (or compounds) in which the corresponding elements are in the highest valency states must be oxidizing agents. These include MnO_4^-, CrO_4^{--} (or $Cr_2O_7^{--}$), Fe^{+++}, etc. These ions can gain electrons and are thus reduced to ions (or compounds) of lower valency, such as Mn^{++}, Cr^{+++} and Fe^{++}. Conversely, the latter are reducing agents and can be oxidized, i.e., they can give up electrons

to suitable oxidizing agents. Substances or ions containing elements of intermediate valencies can be oxidizing agents in some reactions and reducing agents in others. For example, manganese (IV) compounds—MnO_2 or $MnO(OH)_2$—can oxidize such substances as H_2O_2 or nitrites, and can also be oxidized by PbO_2 and certain other oxidizing agents to $HMnO_4$, corresponding to septivalent manganese.

5. Complex Formation. It was stated in Sec. 47 that the elements in the middle of the long periods of the Mendeleyev periodic system have the greatest tendency to form complexes. It is evident from this that complex formation should also play an important part in analysis of Group III cations. The ability of the cations Co^{++}, Ni^{++} and Zn^{++} to form the complex ammines $[Co(NH_3)_6]^{++}$, $[Zn(NH_3)_6]^{++}$ and $[Ni(NH_3)_6]^{++}$ with excess ammonia is used in systematic analysis of Group III cations. The reaction is conducted in the presence of NH_4Cl, which is added so that the solubility product of manganese hydroxide should not be exceeded and so that the Mn^{++} ion should remain in solution together with these complexes. Under these conditions Fe^{+++}, Al^{+++} and Cr^{+++} are precipitated as the hydroxides, because their solubility products are exceeded even at the pH ($\sim$ 9) obtained in a mixture of NH_4OH + NH_4Cl (see Table 10, p. 128), because under the experimental conditions these cations do not form complex ammines. Therefore Group III can be divided into two subgroups by means of a mixture of ammonia and an ammonium salt. An organic base, pyridine (C_5H_5N) can be used instead of ammonia. This base forms complexes of the type $[Me(C_5H_5N)_2]^{++}$, remaining in solution, with Mn^{++}, Zn^{++}, Ni^{++} and Co^{++} ions. At the same time in the presence of pyridine the solution pH is 6.5, and at this pH (see Table 10) Fe^{+++}, Al^{+++}, and Cr^{+++} ions are completely precipitated as the hydroxides.

Other important reactions include the formation of complex cyanides, thyocyanates and thiocyanatomercurates*, used for detection of iron, zinc and cobalt, and the formation of complexes of certain Group III cations with organic reagents—dimethylglyoxime, α-nitroso-β-naphthol, etc.

Finally, in our study of the reactions of Group III cations we shall also consider the use of complex formation for masking interfering ions.

52. Action of the Group Reagent

Group III cations (see Sec. 39) can be precipitated either by hydrogen sulphide or by ammonium sulphide, $(NH_4)_2S$, which is the group reagent. As always in the precipitation of salts of weak acids,

---

* For example, complex salts of the composition $Co[Hg(CNS)_4]$ and $Zn[Hg(CNS)_4]$.

the solution pH is one of the most important conditions. Calculations show that in precipitation by hydrogen sulphide the solution pH must be at least 7.2 for sufficiently complete precipitation of all the Group III cations (p. 183). As solutions of salts of Group III cations have pH < 7 and additional H^+ ions are produced by the reaction, for example

$$Zn^{++} + H_2S \rightleftarrows ZnS + 2H^+$$

a buffer mixture must be added to the solution in order to maintain the pH practically constant (not below 7.2). Of the mixtures generally used in analysis, only the ammonium buffer mixture of pH $= 8$-9 (dependent on the relative concentrations of NH_4OH and NH_4Cl) is completely suitable in this case.

It might seem at first sight that there is no need to provide the appropriate pH in precipitation by ammonium sulphide, because the first stage of hydrolysis

$$(NH_4)_2S + H_2O = NH_4HS + NH_4OH$$

is nearly 100% complete and therefore the $(NH_4)_2S$ solution is itself an ammonium buffer solution with pH $= 9.25$ (p. 216). However, this is not the case. As in the precipitation of Group II cations (Sec. 33), not only must a buffer mixture with the required pH be introduced but it is also necessary to ensure that this value is maintained practically constant, i.e., that the buffer capacity is sufficient. Indeed, the following considerations show that mere addition of $(NH_4)_2S$ to the solution does not suffice in this case.

1. Solutions of salts of Group III cations are acidic owing to hydrolysis; moreover, in systematic analysis HCl is added before precipitation of Groups IV and V by hydrogen sulphide.

If $(NH_4)_2S$ was to be added to such a strongly acidic solution, a large amount would be wasted for neutralization of the acids, and poisonous hydrogen sulphide would be released into the air:

$$(NH_4)_2S + 2HCl = 2NH_4Cl + H_2S\uparrow$$

2. The above equation does not allow for the hydrolysis of $(NH_4)_2S$; in reality ammonium sulphide solutions are mixtures of NH_4OH and NH_4HS as the result of hydrolysis. Taking this into account, we can write the equation in ionic form:

$$NH_4OH + HS^- + 2H^+ = H_2S\uparrow + H_2O + NH_4^+$$

This shows that the reaction of ammonium sulphide with acids consumes NH_4OH and produces NH_4^+ ions.

The same occurs in precipitation of Group III cations:

$$Me^{++} + NH_4OH + HS^- = \downarrow MeS + H_2O + NH_4^+$$

Therefore, although a solution of $(NH_4)_2S$ as such contains equal amounts of NH_4OH molecules and NH_4^+ ions, the above reactions make their concentrations unequal. The concentration ratio becomes less than unity and the pH falls accordingly below 9.25, as follows from the equation (Sec. 16)

$$pH = 14 - 4.75 + \log \frac{[NH_4OH]}{[NH_4^+]}$$

If this fall of pH is substantial, i.e., if the buffer capacity of the solution is inadequate, the precipitation of Group III cations may be incomplete.

3. It should be noted that $(NH_4)_2S$ solutions often contain polysulphides, such as $(NH_4)_2S_2$, formed as the result of oxidation of ammonium sulphide by atmospheric oxygen. The action of acids on polysulphides liberates sulphur:

$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S\uparrow + \downarrow S$$

Contamination of the precipitated sulphides with sulphur is also undesirable.

It follows from all this that ammonium sulphide, although it has the required pH, should not be added directly to acid solutions. The acid must first be neutralized by ammonia. Since addition of ammonia may precipitate Mg^{++}, enough NH_4Cl is also added to ensure that the pH does not rise above 9.3. In other words, before addition of $(NH_4)_2S$ an ammonium buffer mixture must be added in order to raise the buffer capacity of the solution to such an extent as to prevent appreciable changes of pH due to formation of NH_4^+ ions and loss of NH_4OH during precipitation of Group III cations.

It is also useful to add NH_4Cl because it is a coagulant electrolyte which favours coagulation of colloidal sulphides; many of the sulphides, especially NiS, have a great tendency to form colloidal solutions. Coagulation is also assisted if the solution is heated during the precipitation.

Under these conditions (Sec. 39), all the Group III cations, apart from Al^{+++} and Cr^{+++}, are completely precipitated as sulphides. The ions Al^{+++} and Cr^{+++} are precipitated as the hydroxides $Al(OH)_3$ and $Cr(OH)_3$, which are less soluble than the corresponding sulphides. Therefore the solubility products of the hydroxides are reached first and the latter and not the sulphides are precipitated (see p. 205).

It was stated above that Group III cations are precipitated from weakly alkaline solutions, at pH = 9. It must be pointed out that *the solutions must not be strongly alkaline*, for the following reasons: (a) Mg^{++} is completely precipitated together with Group III cations

in strongly alkaline solutions; (b) the amphoteric hydroxides of aluminium and chromium (III) dissolve in strongly alkaline solutions to form AlO_2^- and CrO_2^- ions, which remain in solution together with the cations of Groups II and I.

Therefore *Group III is precipitated by the group reagent*, $(NH_4)_2S$, *in the presence of* NH_4OH *and* NH_4Cl *at* pH $\approx$ 9. *All the Group III cations are precipitated as sulphides, except aluminium and chromium (III), which are precipitated as the hydroxides* $Al(OH)_3$ *and* $Cr(OH)_3$. *Cations of Groups II and I, together with excess* $(NH_4)_2S$ *and other ammonium compounds, remain in solution.*

It must be remembered that $(NH_4)_2S$ solutions often contain SO_4^{--} ions formed as the result of oxidation of S^{--} ions by atmospheric oxygen. Moreover, $(NH_4)_2S$ and the ammonia used for neutralizing the acids may contain CO_3^{--} ions (owing to absorption of CO_2 from the air). Both these anions precipitate the Group II cations. Further, coprecipitation of the latter with the hydroxides of the trivalent Group III cations must be taken into account. Therefore the separation of Groups III and II involves considerable losses of Group II cations, which are partially precipitated with Group III. Under especially unfavourable conditions the Group II cations may even be lost completely. The procedure in such cases is indicated in the description of the analysis of Group II (p. 176).

Let us consider in greater detail the action of acids on the sulphides of Group III cations. As their solubility products are fairly large, they are easily soluble in dilute acids (in contrast to Group IV sulphides, with smaller solubility products). The exceptions are the sulphides of nickel and cobalt, which are almost insoluble (in the cold) in dilute HCl or H_2SO_4. Despite this, Co^{++} and Ni^{++} ions are not precipitated by H_2S in acid solution (for example, at pH $\ll$ 2). The cause of this apparent contradiction is that NiS and CoS can exist in several allotropic forms differing in solubility. The compounds initially formed by precipitation are the least soluble NiS_α and CoS_α, having solubility products of 3×10^{-21} and 7×10^{-23} respectively. In accordance with these solubility products, these forms of the sulphides are easily soluble in acids and are not precipitated by H_2S in acid solution. However, when left to stand in contact with the solution they gradually change into different forms: NiS_γ ($SP = 2 \times 10^{-28}$) and CoS_β ($SP = 2 \times 10^{-27}$), and are no longer soluble in HCl (see Table 13, p. 188). This fact is sometimes used for separating Ni^{++} and Co^{++} from the other Group III cations.

Now examine the action of the group reagent on the individual cations of Group III.

1. Add ammonium sulphide solution to solutions of iron (II), iron (III), manganese, zinc, cobalt and nickel salts. The corresponding

sulphides are precipitated, for example:

$$Fe^{++} + S^{--} = \downarrow FeS$$

$$2Fe^{+++} + 3S^{--} = \downarrow Fe_2S_3$$

$$Mn^{++} + S^{--} = \downarrow MnS \text{ etc.}$$

It is important to remember the colours of the precipitates, as these are important indications in analysis. Precipitates of FeS, Fe_2S_3, CoS and NiS are black, MnS is flesh-coloured*, and ZnS is white. All the Group III sulphides except NiS and CoS dissolve in dilute HCl and H_2SO_4 with evolution of H_2S gas, for example:

$$FeS + 2H^+ = Fe^{++} + H_2S\uparrow$$

$$MnS + 2H^+ = Mn^{++} + H_2S\uparrow \text{ etc.}$$

When Fe_2S_3 is dissolved the Fe^{+++} ion is reduced by the hydrogen sulphide formed to Fe^{++}, and sulphur is precipitated in the form of a white turbidity:

$$Fe_2S_3 + 6H^+ = 2Fe^{+++} + 3H_2S\uparrow$$

$$2Fe^{+++} + H_2S = 2Fe^{++} + 2H^+ + \downarrow S$$

Adding these two equations and cancelling the terms appearing on both sides, we obtain the overall equation for the reaction:

$$Fe_2S_3 + 4H^+ = 2Fe^{++} + \downarrow S + 2H_2S\uparrow$$

CoS and NiS do not dissolve in dilute HCl and H_2SO_4 because they gradually change into less soluble forms. However, this conversion is fairly complete only after prolonged standing of nickel and cobalt sulphides in contact with water; they are appreciably soluble in acids immediately after precipitation.

Complete dissolution of NiS and CoS can be effected by the simultaneous action of an acid and an oxidizing agent such as hydrogen peroxide. The reaction occurs on heating:

$$CoS + 2H^+ + H_2O_2 = Co^{++} + 2H_2O + \downarrow S$$

The action of 6 *N* nitric acid (sp. gr. 1.2) on heating is similar. The reaction is catalytically accelerated by the addition of a few small crystals of KNO_2 or $NaNO_2$. The equation is

$$3CoS + 8HNO_3 = 3Co(NO_3)_2 + \downarrow 3S + 2NO\uparrow + 4H_2O$$

$$3CoS + 8H^+ + 2NO_3^- = 3Co^{++} + \downarrow 3S + 2NO\uparrow + 4H_2O$$

---

* Under certain conditions MnS may also be precipitated in a greenish form.

It is also possible to dissolve the sulphides CoS and NiS by heating with aqua regia (a mixture of 1 volume of concentrated HNO_3 and 3 volumes of concentrated HCl). Of course, nitric acid and aqua regia dissolve all the other Group III sulphides (and hydroxides).

2. Now add $(NH_4)_2S$ to solutions of aluminium and chromium salts. Instead of the sulphides Al_2S_3 and Cr_2S_3, the hydroxides $Al(OH)_3$ (white) and $Cr(OH)_3$ (grey-violet) are precipitated. As already stated, this is due to hydrolysis, as the result of which $(NH_4)_2S$ solutions contain a sufficient concentration of OH^- ions to exceed the solubility products of $Al(OH)_3$ and $Cr(OH)_3$ before the solubility products of Al_2S_3 and Cr_2S_3 are reached. In the case of Cr^{+++} the course of the reaction may be represented as follows:

$$6(NH_4)_2S + 6H_2O = 6NH_4HS + 6NH_4OH$$
$$Cr_2(SO_4)_3 + 6NH_4OH = 2Cr(OH)_3 + 3(NH_4)_2SO_4$$

$$Cr_2(SO_4)_3 + 6(NH_4)_2S + 6H_2O = \downarrow 2Cr(OH)_3 + 6NH_4HS + 3(NH_4)_2SO_4$$

The ionic form of the equation is

$$2Cr^{+++} + 6S^{--} + 6H_2O = \downarrow 2Cr(OH)_3 + 6HS^-$$

As some of the HS^- ions formed in this reaction are converted into H_2S as the result of further hydrolysis, the following reaction also occurs partially:

$$2Cr^{+++} + 3S^{--} + 6H_2O = \downarrow 2Cr(OH)_3 + \uparrow 3H_2S$$

Write the corresponding equations for Al^{+++}.

The sulphides of the remaining Group III cations are less soluble than the corresponding hydroxides. Because of this the solubility products of the sulphides are reached before those of the hydroxides and therefore the sulphides and not the hydroxides are precipitated by $(NH_4)_2S$.

The $Al(OH)_3$ and $Cr(OH)_3$ precipitates are soluble in dilute acids.

Finally, examine the action of hydrogen sulphide on solutions of salts of Group III cations. Add a solution of H_2S in water to a solution of $MnSO_4$ or $FeSO_4$. Are MnS or FeS precipitated? Explain (see Sec. 39).

53. Reactions of the Al^{+++} Cation

The Al^{+++} ion is colourless in aqueous solutions. To study its reactions, take a solution of alum, $KAl(SO_4)_2 \cdot 12H_2O$, or $AlCl_3$.

1. Caustic alkalies, KOH or NaOH, give a white precipitate of $Al(OH)_3$ when added *drop by drop* to solutions of aluminium salts:

$$Al^{+++} + 3OH^- = \downarrow Al(OH)_3$$

The precipitate is amphoteric (Sec. 45) and dissolves in both acids and alkalies:

$$Al(OH)_3 + 3H^+ = Al^{+++} + 3H_2O$$

$$\underset{(H_3AlO_3)}{Al(OH)_3} + OH^- = AlO_2^- + 2H_2O$$

Written in molecular form, the equation for the reaction with caustic soda is

$$\underset{(H_3AlO_3)}{Al(OH)_3} + NaOH = NaAlO_2 + 2H_2O$$

The compounds formed by the action of alkalies on $Al(OH)_3$ are known as *aluminates.*

The precipitation of $Al(OH)_3$ is complete at pH $\approx$ 5 (see Sec. 45); on further addition of alkali to pH $>$ 10 $Al(OH)_3$ dissolves to form AlO_2^- ions. It follows that in order to obtain a precipitate of $Al(OH)_3$ from a solution of aluminate and then to obtain Al^{+++} cations we must lower the solution pH by means of an acid. To confirm this, add *single drops* of dilute HCl to the aluminate solution obtained in the preceding experiments. A precipitate of $Al(OH)_3$ is formed first. On addition of more acid (i.e., on decrease of pH) the precipitate dissolves again. The reactions correspond to the equations

$$AlO_2^- + H^+ + H_2O = Al(OH)_3$$

$$Al(OH)_3 + 3H^+ = Al^{+++} + 3H_2O$$

Adding them, we obtain the overall equation for the reaction taking place in the conversion of AlO_2^- anions into Al^{+++} cations:

$$AlO_2^- + 4H^+ = Al^{+++} + 2H_2O$$

To stop the reaction at the stage of $Al(OH)_3$ formation we must use a reagent which lowers the solution pH but not below 5. A suitable reagent is NH_4Cl. The NH_4^+ ions combine with OH^- ions and thereby lower the pH. However, the NH_4OH ion which is formed, together with the excess NH_4Cl, provides an ammonium buffer mixture of pH $\approx$ 9 (if the concentrations of the two components are equal). Therefore in this case the precipitate does not redissolve and the reaction stops at the $Al(OH)_3$ stage. The equation is

$$AlO_2^- + 2H_2O + NH_4^+ = \downarrow Al(OH)_3 + NH_4OH$$

This reaction is often used for detection of Al^{+++} in systematic analysis. Study it experimentally. To a solution of an aluminate (prepared as described above) add a saturated NH_4Cl solution (or a small amount of the solid salt) and heat for a few minutes. $Al(OH)_3$ is precipitated in the form of white gelatinous flakes, which often float to the top.

The test is reliable only if the solution is heated (boiled) for a long time until nearly all the ammonia has been removed. $Al(OH)_3$

is not precipitated if the ammonia which may form by the reaction of the alkali in solution with NH_4Cl is present in sufficient excess to raise the pH above 10. It is therefore more reliable to precipitate aluminium hydroxide by the action of NH_4OH after AlO_2^- ions have been first converted into Al^{+++} cations by addition of HCl until the solution is acid (see 2 below).

2. **Ammonium hydroxide, NH_4OH,** also precipitates Al^{+++} as $Al(OH)_3$, which is partially soluble in excess* reagent (owing to the amphoteric properties of aluminium hydroxide). As the solubility product of $Al(OH)_3$ is very small and Al^{+++} does not form complexes with ammonia, $Al(OH)_3$ is not soluble in ammonium salts. Therefore Al^{+++} is precipitated by a mixture of ammonia and an ammonium salt.

This is also evident from the fact that the precipitation of $Al(OH)_3$ is complete even at pH = 5, whereas the pH of NH_4OH + NH_4Cl mixtures is between 8 and 10, dependent on the relative concentrations of the components.

3. **Salts of weak acids,** such as Na_2CO_3, Na_2SO_3, KNO_2, etc., precipitate Al^{+++} as $Al(OH)_3$ because solutions of these salts have a sufficient concentration of OH^- ions as the result of hydrolysis, for example:

$$3Na_2CO_3 + 2AlCl_3 + 3H_2O = \downarrow 2Al(OH)_3 + 6NaCl + 3CO_2\uparrow$$

or

$$3CO_3^{--} + 2Al^{+++} + 3H_2O = \downarrow 2Al(OH)_3 + 3CO_2\uparrow$$

It will be remembered that the group reagent has the same action on the Al^{+++} ion.

4. **Sodium acetate, CH_3COONa,** gives white flocculent precipitates of basic salts with solutions of aluminium salts:

$$Al_2(SO_4)_3 + 6CH_3COONa = 2(CH_3COO)_3Al + 3Na_2SO_4$$

$$2(CH_3COO)_3Al + 4H_2O = \downarrow 2CH_3COO(OH)_2Al + 4CH_3COOH$$

The ionic equation is

$$Al^{+++} + 3CH_3COO^- + 2H_2O \rightleftarrows \downarrow CH_3COO(OH)_2Al + 2CH_3COOH$$

The solution should be greatly diluted with water and boiled to increase hydrolysis.

5. **Disodium hydrogen phosphate, Na_2HPO_4,** precipitates Al^{+++} in the form of white $AlPO_4$, soluble in strong acids but *practically insoluble in acetic acid.* The equation is

$$AlCl_3 + Na_2HPO_4 \rightleftarrows \downarrow AlPO_4 + 2NaCl + HCl$$

---

* It dissolves completely only if a very large excess of concentrated NH_4OH is present.

The HCl formed reacts with excess Na_2HPO_4:

$$HCl + Na_2HPO_4 = NaCl + NaH_2PO_4$$

Therefore a phosphate buffer mixture ($NaH_2PO_4 + Na_2HPO_4$) maintaining the pH at about 7 is formed in solution; this is quite adequate for complete precipitation of $AlPO_4$. Adding the above equations we obtain the overall equation for the reaction:

$$AlCl_3 + 2Na_2HPO_4 = \downarrow AlPO_4 + NaH_2PO_4 + 3NaCl$$

or

$$Al^{+++} + 2HPO_4^{--} = \downarrow AlPO_4 + H_2PO_4^-$$

It must be noted that Na_2HPO_4 precipitates the aluminium ion as the phosphate $AlPO_4$ and not the acid phosphate $Al_2(HPO_4)_3$. The reason is that the reagent used, Na_2HPO_4, contains (in addition to a large amount of HPO_4^{--} ions) some PO_4^{---} ions formed from the latter:

$$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---} \quad (K_3 = 2.2 \times 10^{-13})$$

Although the PO_4^{---} ion concentration is very low, the solubility product of $AlPO_4$ is reached first because of the much lower solubility of this salt, and it is therefore precipitated. As soon as the precipitation has started the PO_4^{---} ions removed from the solution are immediately replaced owing to further dissociation of HPO_4^{--} ions, so that almost all the Al^{+++} ions are precipitated in the form of $AlPO_4$.

In contrast to Al^{+++}, the cations of Group II are precipitated by the same reagent as the acid phosphates $BaHPO_4$, $CaHPO_4$, etc., because the solubility products of these salts are reached first. However, the neutral salts such as $Ba_3(PO_4)_2$ can also be obtained if the reaction is conducted in the presence of alkali; the OH^- ions of the latter react with HPO_4^{--} ions:

$$HPO_4^{--} + OH^- = PO_4^{---} + H_2O$$

This raises the PO_4^{---} and lowers the HPO_4^{--} concentration so much that the solubility products of the neutral phosphates such as $Ba_3(PO_4)_2$ are reached first.

All the foregoing demonstrates yet again the principle of fractional precipitation (Sec. 27): whenever several different sparingly soluble compounds can be formed in a reaction, the one actually precipitated is the one whose solubility product is reached first. This also applies to the action of salts of weak acids on the Al^{+++} ion (see above), of $K_2Cr_2O_7$ solution on Ba^{++}, etc.

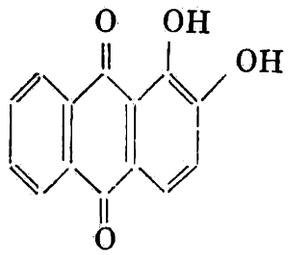
6. Alizarin* forms a compound known as "aluminium lake", bright red and insoluble, with aluminium hydroxide. This is best suited for a spot test on a strip of filter paper. Put a drop of the solution tested for Al^{+++} (for example, $AlCl_3$) on the paper and hold it for 1-2 minutes over an open flask containing concentrated ammonia. This precipitates Al^{+++} as $Al(OH)_3$. Next treat the moist spot with a drop of alcoholic alizarin solution and again expose it to ammonia vapour. Alizarin forms a red-violet compound with NH_3. To eliminate this colour, which masks the red colour given by Al^{+++}, dry the paper carefully over a burner flame or an electric hot-plate. The ammonia is volatilized and the violet colour changes to a pale yellow background against which the rose-red spot formed by the aluminium lake is clearly visible.

Fe^{+++} and certain other ions interfere. The detection of Al^{+++} in their presence is described later (Sec. 116).

7. Aluminon** also forms a red lake with $Al(OH)_3$. To carry out the test, add a little of 0.1% aqueous aluminon solution to 1-2 ml of an aluminium salt solution slightly acidified with CH_3COOH and warm; then add NH_4OH (until the liquid smells of ammonia) and $(NH_4)_2CO_3$ solution. Red flakes of the aluminium lake prove the presence of Al^{+++}.

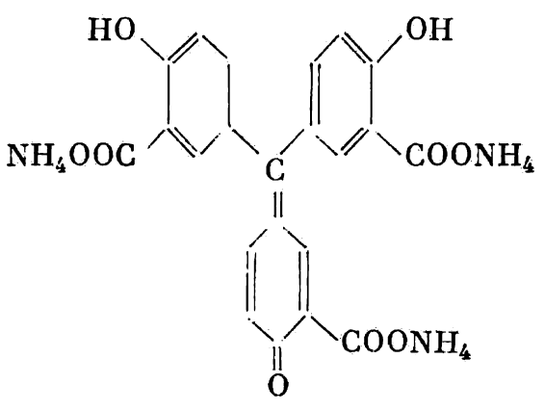
---

* The formula of alizarin (1.2-dihydroxyanthraquinone) is



The lake formed in the reaction of alizarin with aluminium hydroxide is of indefinite composition. It is probably an adsorption compound of aluminium hydroxide and alizarin.

** The formula of aluminon (the ammonium salt of aurin tricarboxylic acid) is



This test is highly sensitive. It should be remembered, however, that Fe^{+++}, Cr^{+++} and Ca^{++} also give red lakes with aluminon. In contrast to the lake formed with Al^{+++}, the lake formed with Cr^{+++} is decomposed by NH_4OH and the Ca^{++} lake by $(NH_4)_2CO_3$. The Fe^{+++} ion must be completely removed before the test (by means of excess alkali; the solution containing AlO_2^- is then acidified with CH_3COOH).

8. **Morin*** gives a fine green fluorescence with solutions of aluminium salts.

To carry out the test, add CH_3COOH and about 5 ml of water to a few drops of an aluminium salt solution, followed by 2-3 drops of morin solution. If the fluorescence is weak, slightly warm the test tube and then cool it by immersion in cold water. The test is highly sensitive, but the fluorescence is difficult to see by electric light.

9. **Microcrystalloscopic Test.** Put a small crystal of $KHSO_4$ into a drop of an aluminium salt solution and warm it gently until most of the liquid has evaporated. Examine the crystals of alum, $KAl(SO_4)_2 \cdot 12H_2O$, under the microscope. They are of the form shown in Fig. 29. At a high concentration dendrites (tree-like forms) may occur instead. If all the liquid has evaporated, when the alum crystals become overgrown with crystals of other substances and are indistinguishable, put a small drop of water at the edge of the specimen or merely moisten the dry residue with the breath. The other substances then dissolve and the alum crystals become more distinct.

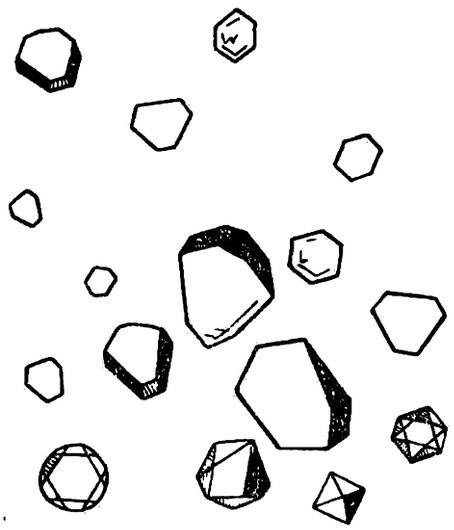


Fig. 29. Alum crystals

If it is required to use this test for detecting Al^{+++} in a solution containing other Group III cations, a small amount of the solution should first be treated at the boil with *excess* of caustic alkali. This dissolves Al^{+++} in the form of aluminate and it can then be detected by this test after the solution has been *slightly* acidified with HCl (an excess of acid is harmful). The detectable minimum is 0.35 μg Al^{+++}. The test is much more sensitive if caesium sulphate is used instead of $KHSO_4$ (0.08 μg Al^{+++}).

10. **Dry-Way Test.** Solid aluminium compounds, after treatment with *very dilute* $Co(NO_3)_2$ solution and calcination, are coloured blue

---

* Morin is a pigment found in yellow wood (*Morus tinctura*). Its composition corresponds to the formula $C_{15}H_{10}O_7 \cdot 2H_2O$, and the compound formed with aluminium is $Al(C_{15}H_9O_7)_3$.

owing to the formation of cobalt aluminate, $Co(AlO_2)_2$:

$$2Al_2(SO_4)_3 + 2Co(NO_3)_2 = 2Co(AlO_2)_2 + 6SO_3\uparrow + 4NO_2\uparrow + O_2\uparrow$$

Cobalt aluminate is sometimes called "Thenard's blue".

54. Reactions of Chromium Ions

Chromium forms two series of stable salts: salts of chromic oxide and salts of chromic (and dichromic) acid. Solutions of salts of chromic oxide (chromic salts) contain chromium as the trivalent cation Cr^{+++}. Various oxidizing agents readily convert trivalent chromium into the sexivalent state to give anions of chromic acid, CrO_4^{--} (chromate ions) or of dichromic acid, $Cr_2O_7^{--}$ (dichromate ions).

Solutions of chromic salts are green or violet; those of chromates are yellow, and of bichromates, orange.

Reactions of the Cr^{+++} *cation*

1. **Caustic alkalies, NaOH and KOH,** form a grey-violet precipitate or $Cr(OH)_3$ with Cr^{+++} ions; the hydroxide is amphoteric. Confirm this by experiment. The equations for the reactions are analogous to the corresponding equations for the reactions of the Al^{+++} ion. The chromites $NaCrO_2$ and $KCrO_2$ formed by the action of alkalies on $Cr(OH)_3$ are bright green. In contrast to aluminates, they decompose on boiling (owing to hydrolysis) to form $Cr(OH)_3$ (test this):

$$NaCrO_2 + 2H_2O = \downarrow Cr(OH)_3 + NaOH$$

2. **Ammonia and salts of weak acids** [Na_2CO_3, $(NH_4)_2S$, etc.] also precipitate Cr^{+++} as $Cr(OH)_3$. The precipitate is somewhat soluble in excess ammonia.

Since $Cr(OH)_3$ is precipitated completely at pH $\approx$ 6 (see Table 10, p. 128), it is also completely precipitated by ammonium buffer mixture (NH_4OH + NH_4Cl) giving a pH value of 8-10 (compare Al^{+++}).

3. **Sodium acetate, CH_3COONa,** does not give (on boiling) a precipitate with Cr^{+++} owing to the formation of water-soluble acetate complex (distinction from Al^{+++} and Fe^{+++} ions). In the presence of large amounts of Al^{+++} and Fe^{+++} ions Cr^{+++} may be coprecipitated as the basic acetate.

4. **Disodium hydrogen phosphate, Na_2HPO_4,** forms a greenish precipitate of $CrPO_4$ with Cr^{+++}. The reaction is similar to that with Al^{+++} (Sec. 53, 5). The precipitate is soluble in mineral acids and in alkalies.

5. **Dry-Way Test (Bead Formation).** Prepare a precipitate of $Cr(OH)_3$ by one of the above methods and filter it off. Take a glass

rod with a platinum wire with its end bent into a loop. Heat the tip of the wire to redness and touch solid borax* $Na_2B_4O_7 \cdot 10H_2O$ or (preferably) sodium ammonium phosphate (microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$) with it. Heat the adhering crystals in the burner flame until the mass ceases to froth. Take the wire with its bead out of the flame and let it cool. Now take a little of the $Cr(OH)_3$ precipitate on the bead and heat it again as before. When cool, hold the bead up to the light. In the presence of chromium the bead is emerald green in colour. The colour of the bead is due to the formation of chromium phosphate, $CrPO_4$, or chromium metaborate**, $Cr(BO_2)_3$. The reactions are

$$3NaNH_4HPO_4 + 2Cr(OH)_3 = 2CrPO_4 + Na_3PO_4 + 3NH_3\uparrow + 6H_2O\uparrow$$

$$3Na_2B_4O_7 + 2Cr(OH)_3 = 2Cr(BO_2)_3 + 6NaBO_2 + 3H_2O\uparrow$$

After this experiment remcve the bead from the platinum wire. To do this, heat it to redness again and shake off the hot drop by tapping the glass rod gently. Save the $Cr(OH)_3$ precipitate for a later experiment (fusion with sodium carbonate and sodium nitrate).

6. Oxidation of trivalent chromium to the sexivalent state may be effected by various oxidizing agents, such as H_2O_2, Na_2O_2, Cl_2, Br_2, $KMnO_4$, $(NH_4)_2S_2O_8$, etc. Oxidation in alkaline solution yields CrO_4^{--} ions. Oxidation in acid solution leads to formation of $Cr_2O_7^{--}$ ions. The reason is that these ions are interconverted when the H^+ ion concentration changes:

$$2CrO_4^{--} + 2H^+ \rightleftarrows 2HCrO_4^- \rightleftarrows Cr_2O_7^{--} + H_2O$$

This equation shows that when the solution is acidified both equilibria should shift towards formation of $Cr_2O_7^{--}$ ions, whereas if the solution is made alkaline (with removal of H^+ ions) the shift is in the direction of CrO_4^{--} formation.

Confirm this experimentally. Add an acid to a solution of K_2CrO_4. An orange colour appears, characteristic of $Cr_2O_7^{--}$ ions. Next add an alkali to $K_2Cr_2O_7$ solution. What does the colour change indicate?

In the light of all this, let us examine both cases of oxidation separately.

(a) *Oxidation in alkaline solution* is usually effected by hydrogen peroxide or sodium peroxide. For example, let us consider oxidation by means of H_2O_2.

We know that in alkaline solution trivalent chromium exists in the form of chromites, such as $NaCrO_2$. Therefore the following substances are involved in the reaction:

$$NaCrO_2 + H_2O_2 + NaOH \longrightarrow Na_2CrO_4 + H_2O$$

---

* Sodium tetraborate, a salt of tetraboric acid $H_2B_4O_7$.

** A salt of metaboric acid, HBO_2.

The following transfer of electrons takes place* in the reaction:

$$\begin{array}{rl} Cr^{+III} - 3e = Cr^{+VI} & \mid 2 \\ O_2^{--} + 2e = 2O^{--} & \mid 3 \end{array}$$

Therefore the equation for the reaction is

$$2NaCrO_2 + 3H_2O_2 + 2NaOH = 2Na_2CrO_4 + 4H_2O$$

or, in ionic form

$$2CrO_2^- + 3H_2O_2 + 2OH^- = 2CrO_4^{--} + 4H_2O$$

Add alkali to a solution of a chromic salt until the $Cr(OH)_3$ precipitate formed redissolves; then add H_2O_2 and heat the solution until the colour changes from green to yellow (colour of CrO_4^{--} ions). Keep the solution for further experiments. We will use this reaction for separating chromium from Fe^{+++} and Mn^{++} ions.

Sodium peroxide and bromine (or chlorine) water act similarly to H_2O_2; for example

$$2CrO_2^- + 3Br_2 + 8OH^- = 2CrO_4^{--} + 6Br^- + 4H_2O$$

(b) *Oxidation in acid solution* may be effected by means of $KMnO_4$, $(NH_4)_2S_2O_8$, and some other strong oxidizing agents. For example, let us examine the action of ammonium persulphate, $(NH_4)_2S_2O_8$, on chromic salts.

The equation for the reaction is**

$$2Cr^{+++} + 3S_2O_8^{--} + 7H_2O = Cr_2O_7^{--} + 6SO_4^{--} + 14H^+$$

To carry out this reaction, take 1-2 ml of $(NH_4)_2S_2O_8$ solution in a test tube, and add a little 2 *N* H_2SO_4 followed by a few drops of a solution of a silver salt (as catalyst). To this oxidizing mixture add 1-2 ml of $Cr_2(SO_4)_3$ or $Cr(NO_3)_3$ solution (*not* $CrCl_3$). Note the colour change when the solution is heated. Keep the solution for further experiments.

---

* See p. 246.

** As a fictitious value (+7) is found by calculation for the valency of sulphur in $(NH_4)_2S_2O_8$ (sulphur, being an element in Group VI of the periodic system, cannot have a valency greater than 6), in working out the electron transfer scheme we must take into account that the $S_2O_8^{--}$ ion is converted into two SO_4^{--} ions, i.e., gains two electrons, in the reaction:

$$\begin{array}{rl} 2Cr^{+++} - 6e = 2Cr^{+VI} & \mid 1 \\ S_2O_8^{--} + 2e = 2SO_4^{--} & \mid 3 \end{array}$$

This gives the equation in the text.

The action of potassium permanganate on Cr^{+++} is analogous to that of persulphate:

$$Cr_2(SO_4)_3 + 2KMnO_4 + 5H_2O = \downarrow 2MnO(OH)_2 + K_2Cr_2O_7 + 3H_2SO_4$$

or

$$2Cr^{+++} + 2MnO_4^- + 5H_2O = \downarrow 2MnO(OH)_2 + Cr_2O_7^{--} + 6H^+$$

The reaction, which takes place on heating, is accompanied by the formation of a brown precipitate of manganous acid, $MnO(OH)_2$*.

To ensure that there is enough permanganate to oxidize all the reducing agents present in the solution, including Cr^{+++} ions, it should be added until the supernatant liquid remains a purple-violet colour (at the end of heating), indicating an excess of $KMnO_4$. At this stage the $MnO(OH)_2$ precipitate is filtered off and the cooled solution is tested for $Cr_2O_7^{--}$ by the perchromic acid test (see p. 274, 3). This method can be used for the detection of chromium in the presence of all the other Group III cations.

(c) *Dry-way oxidation.* It is also possible to oxidize Cr^{III} to Cr^{VI} in the dry way, for example by fusion of a chromic salt with a mixture of sodium carbonate and sodium nitrate. The oxidizing agent in this reaction is $NaNO_3$, which is reduced to $NaNO_2$ as follows:

$$\begin{array}{rl} Cr^{+III} - 3e = Cr^{+VI} & \mid 2 \\ N^{+V} + 2e = N^{+III} & \mid 3 \end{array}$$

Therefore the equation for the reaction is

$$2Cr(OH)_3 + 3NaNO_3 + 2Na_2CO_3 = 2Na_2CrO_4 + 3NaNO_2 + 3H_2O + 2CO_2\uparrow$$

Reactions of the CrO_4^{--} *and* $Cr_2O_7^{--}$ *anions*

1. Formation of Sparingly Soluble Salts. The anion CrO_4^{--} forms sparingly soluble precipitates with Pb^{++}, Ag^+ and Ba^{++}; this is used for detection and separation of chromates.

The equations are:

$$CrO_4^{--} + Pb^{++} = \underset{\text{Yellow}}{\downarrow PbCrO_4}$$

$$CrO_4^{--} + Ba^{++} = \underset{\text{Yellow}}{\downarrow BaCrO_4}$$

$$CrO_4^{--} + 2Ag^+ = \underset{\text{Brick-red}}{\downarrow Ag_2CrO_4}$$

---

* $MnO(OH)_2$ is formed here, rather than a manganous salt as is usually the case in oxidation by permanganate in acid solution, because the solution is not sufficiently acidic. Too much acid should not be used in this case.

The solution must be acidified with acetic acid for these reactions*.

2. **Benzidine**** is oxidized by sexivalent chromium ions in the presence of acetic acid to give a blue product. Trivalent chromium can be detected in this way if Cr^{+++} is first oxidized to CrO_4^{--} by H_2O_2 or Na_2O_2. This reaction, proposed by N. A. Tananaev, is used as a spot test. Put a drop of the solution obtained in the reaction with H_2O_2 (p. 270) on a strip of filter paper and apply a drop of benzidine acetate. The spot turns blue owing to the oxidation of benzidine*** by CrO_4^{--} ions. The test detects 0.25 μg of chromium. The dilution limit is 1 : 200,000.

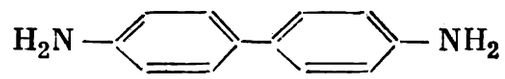
This reaction can be used for fractional detection of Cr^{+++} in the presence of any other cations.

The test must be carried out on a watch glass (or a crucible lid). Put 3-5 drops of the unknown solution on this, add a little sodium peroxide, and warm gently. Cr^{+++} ions are then oxidized to CrO_4^{--}. Dilute the mixture with 2-3 drops of water and introduce into it a tip of a glass tube drawn out to a capillary to withdraw a small amount of the liquid and precipitate. Touch a piece of filter paper with the capillary tip and leave it there until a watery patch a few millimetres across has formed around the precipitate which remains in the middle. The patch contains CrO_4^{--} and the precipitate consists of various hydroxides, including $Co(OH)_3$ and $MnO(OH)_2$. Draw the tip of a capillary containing benzidine solution around the edges of the damp spot. If the unknown solution contains chromium, a blue ring appears at the edges of the spot. Care must be taken not to allow the benzidine solution to reach the middle of the spot, because it might then turn blue even in the absence of CrO_4^{--} owing to the presence of $Co(OH)_3$ and $MnO(OH)_2$, which also oxidize benzidine, in the precipitate. This means that *the test is conclusive only if there is a colourless zone between the blue ring and the precipitate.*

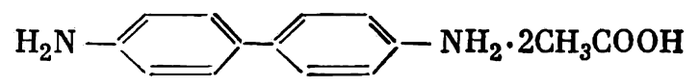
---

* The test for CrO_4^{--} with Ag^+ cannot be used in the presence of Cl^- ions, as the less soluble AgCl would be precipitated first. Similarly, SO_4^{--} ions interfere with detection of CrO_4^{--} by means of Ba^{++} or Pb^{++} ions, owing to precipitation of $BaSO_4$ or $PbSO_4$.

** The formula of benzidine is



Benzidine acetate has the formula



*** The equation for the oxidation of benzidine is given in the footnote on p. 283 for the simpler case of oxidation by $MnO(OH)_2$.

3. Formation of Perchromic Acid*, H_2CrO_6. To 1-2 ml of the acid dichromate solution obtained by the oxidation of Cr^{+++} ions by persulphate or permanganate add about 1 ml of diethyl ether or amyl alcohol followed by a few drops of H_2O_2 and shake the test tube immediately. The lighter top layer of ether or amyl alcohol is coloured a fine blue owing to the formation of perchromic acid:

$$Cr_2O_7^{--} + 4H_2O_2 + 2H^+ = 2H_2CrO_6 + 3H_2O$$

Ether or amyl alcohol is used in this test because H_2CrO_6 rapidly decomposes in aqueous solution to evolve oxygen and form Cr^{+++}.

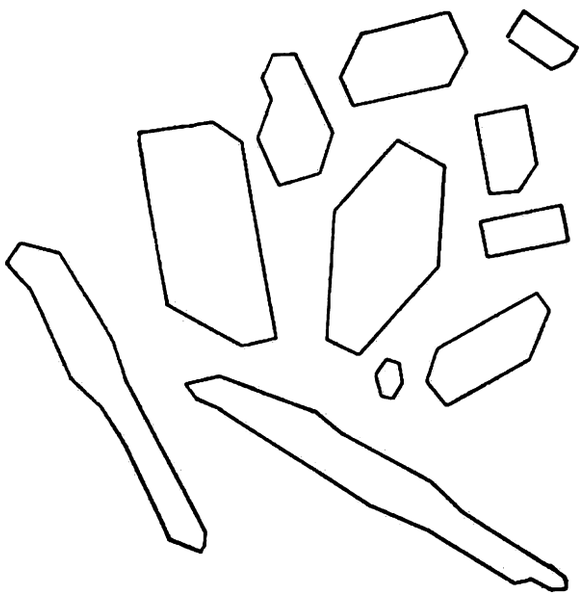


Fig. 30. Crystals of $Ag_2Cr_2O_7$

Solutions of chromium peroxide in the above named solvents are much more stable. When using this most characteristic test for detection of chromium, remember that *it works only in acid solution.* Therefore if Cr^{III} had been oxidized to Cr^{VI} in alkaline solution it is necessary to acidify with H_2SO_4. Care must also be taken *to keep the solution at room temperature*, because H_2CrO_6 decomposes instantly in hot solution.

4. Reduction of Cr^{VI} to Cr^{III} may be effected by various reducing agents, such as Na_2SO_3, H_2S, ethyl alcohol, (C_2H_5OH), ferrous salts, and similar substances in *acid solution.* For example, add a few drops of Na_2SO_3 solution to $K_2Cr_2O_7$ solution acidified with H_2SO_4, and explain the colour change which takes place. The equation for the reaction is

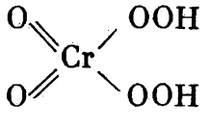
$$K_2Cr_2O_7 + 3Na_2SO_3 + 4H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 3Na_2SO_4 + 4H_2O$$

or

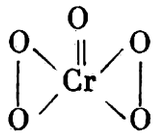
$$Cr_2O_7^{--} + 3SO_3^{--} + 8H^+ = 2Cr^{+++} + 3SO_4^{--} + 4H_2O$$

---

* The structural formula of H_2CrO_6 is



Some authors attribute the formula H_3CrO_8 or H_7CrO_{10} to the reaction product, or consider it to be a peroxide of chromium of the composition



Because of its oxidizing properties, a mixture of $K_2Cr_2O_7$ and concentrated H_2SO_4 (known as chromic mixture) is widely used in chemical laboratories, in particular for washing glassware and removing grease from glass surfaces.

5. Microcrystalloscopic Test for $Cr_2O_7^{--}$. Add a small fragment of a solid chromate to a drop of $AgNO_3$ solution slightly acidified with acetic acid and examine under the microscope the large orange or brown-red crystals of $Ag_2Cr_2O_7$ formed (Fig. 30). A large amount of Cl^- ions interferes with the reaction. The detectable minimum is 0.025 μg of Cr^{VI}.

To detect chromium in a chromic salt by this test, Cr^{III} is first oxidized by the action of H_2O_2 in alkaline solution or by fusion with sodium carbonate and nitrate. In the former case the solution must be evaporated to dryness.

55. Reactions of Iron Cations

Iron forms two series of salts, ferric and ferrous. Solutions of ferric salts contain trivalent Fe^{+++} cations, while ferrous salts contain bivalent Fe^{++}. As the reactions of these ions are entirely different, we shall consider them separately.

Reactions of the Fe^{+++} *cation*

Solutions of ferric salts are yellow or red-brown. The most important reactions of the Fe^{+++} ion are given below.

1. Caustic alkalies (NaOH and KOH) and NH_4OH precipitate red-brown $Fe(OH)_3$ from solutions containing Fe^{+++} ions:

$$Fe^{+++} + 3OH^- = \downarrow Fe(OH)_3$$

In contrast to $Al(OH)_3$ and $Cr(OH)_3$, ferric hydroxide is not amphoteric and therefore does not dissolve in excess alkali (test this). As the solubility product of $Fe(OH)_3$ is very small ($SP = 3.8 \times 10^{-38}$), ferric hydroxide is also insoluble in ammonium salts and can be obtained by the action of ammonia on solutions of ferric salts in the presence of ammonium salts.

2. Sodium acetate, CH_3COONa, forms ferric acetate, $(CH_3COO)_3Fe$, with Fe^{+++} ions in the cold (the solution turns brown-red).

If the solution is then diluted with water and heated to boiling, hydrolysis of $(CH_3COO)_3Fe$ is intensified and leads to the formation of a basic salt in the form of a brown precipitate:

$$(CH_3COO)_3Fe + 2H_2O \rightleftarrows \downarrow CH_3COO(OH)_2Fe + 2CH_3COOH$$

It will be remembered that Al^{+++} reacts similarly with CH_3COONa, except that $CH_3COO(OH)_2Al$ is white. Other Group III cations do not form precipitates with CH_3COONa*.

* See p. 269, 3, concerning the behaviour of Cr^{+++}.

3. Carbonates of the alkali metals and ammonium carbonate give brown precipitates of the basic salts with Fe^{+++}; when boiled, these are converted into the hydroxide.

4. Ammonium and potassium thiocyanates*, NH_4CNS and KCNS, form ferric thiocyanate $Fe(CNS)_3$ with Fe^{+++}; this is a water-soluble compound of a blood-red colour**:

$$Fe^{+++} + 3CNS^- \rightleftarrows Fe(CNS)_3$$

As this reaction is reversible, excess of the reagent intensifies the colour. This is one of the most important and most sensitive tests for the Fe^{+++} ion. However, it is not always reliable because a number of substances which form complexes with Fe^{+++} ions prevent the colour formation. These include fluorides, as the F^- ion forms the complex $[FeF_6]^{---}$ ion, very weakly dissociated, with Fe^{+++}. Confirm this experimentally by adding NH_4CNS followed by NH_4F or NaF to a solution of a ferric salt. The colour due to formation of $Fe(CNS)_3$ disappears owing to the reaction

$$Fe(CNS)_3 + 6F^- = [FeF_6]^{---} + 3CNS^-$$

The same occurs on addition of phosphoric acid, oxalates, tartrates, citrates, etc.

5. Potassium ferrocyanide, $K_4[Fe(CN)_6]$, forms a dark blue precipitate of Prussian blue with Fe^{+++} ions:

$$4Fe^{+++} + 3[Fe(CN)_6]^{====} \downarrow Fe_4[Fe(CN)_6]_3$$

This most important test for the Fe^{+++} ion works better if the solution is moderately acid. Too much acid is not advisable, because the precipitate redissolves, as in a large excess of the reagent. Alkalies decompose Prussian blue to form ferric hydroxide, $Fe(OH)_3$.

6. Disodium hydrogen phosphate, Na_2HPO_4, forms a pale yellow precipitate of $FePO_4$ with Fe^{+++}, soluble in strong acids but insoluble *in acetic acid* (test this). The equation is

$$Fe^{+++} + 2HPO_4^{--} = \downarrow FePO_4 + H_2PO_4^- \text{ (compare } Al^{+++})$$

7. Oxidation-Reduction Reactions. As the Fe^{+++} ion can be reduced to Fe^{++}, it is an oxidizing agent.

For example, when hydrogen sulphide is passed through an acidified solution of a ferric salt, H_2S is oxidized to sulphur which is precipitated in the form of a white turbidity:

$$2Fe^{+++} + H_2S = 2Fe^{++} + 2H^+ + \downarrow S$$

---

* Salts of thiocyanic acid, HCNS.

** In addition to $Fe(CNS)_3$, a series of thiocyanate complexes ranging from $[Fe(CNS)]^{++}$ to $[Fe(CNS)_6]^{---}$ is formed in this reaction.

It will be remembered that this reaction also occurs when Fe_2S_3 precipitates are dissolved in acids (Sec. 52). The Fe^{+++} ion also oxidizes Sn^{++} to Sn^{++++} and I^- to I_2:

$$Sn^{++} + 2Fe^{+++} = Sn^{++++} + 2Fe^{++}$$

$$2I^- + 2Fe^{+++} = I_2 + 2Fe^{++}$$

To demonstrate the latter reaction, add a ferric salt to KI solution. The liquid turns brown. Now add a small amount of benzene, C_6H_6 (or ligroin), to the solution and shake the test tube. As I_2 is more soluble in these solvents than in water, most of the iodine passes into the solvent layer and colours it violet (the characteristic colour of iodine solutions in benzene or ligroin).

However, Fe^{+++} is a *weak* oxidizing agent, i.e., one of low chemical activity. Therefore it can oxidize only the stronger reducing agents, like those named above. Weaker reducing agents, such as Br^-, Cl^-, etc., are not oxidized by Fe^{+++}*.

8. Detection of Fe^{III} by the Grinding Method (F. M. Flavitsky's method). Put a few small crystals of solid $Fe_2(SO_4)_3$ in a small porcelain basin (or on a porcelain tile) and grind them with the narrow end of a porcelain pestle with an approximately equal amount of solid NH_4CNS. The reaction mixture turns red-brown owing to the formation of $Fe(CNS)_3$. To detect Fe^{+++} in solution, a few drops must be evaporated to dryness with 1-2 drops of 2 *N* H_2SO_4; the dry residue is cooled and tested as above.

Reactions of the Fe^{++} *cation*

Ferrous salts are pale green in solution. Dilute solutions are colourless.

1. Caustic alkalies, NaOH and KOH, in the absence of air precipitate Fe^{++} as a white precipitate of $Fe(OH)_2$; under normal conditions the precipitate is a dingy green colour:

$$Fe^{++} + 2OH^- = \downarrow Fe(OH)_2$$

The precipitate is oxidized rapidly in air and changes colour; this is observed more conveniently if the precipitate is filtered off. The final oxidation product is $Fe(OH)_3$. The $Fe(OH)_2$ precipitate is soluble in acids but not in alkalies.

2. Ammonia, NH_4OH, also precipitates $Fe(OH)_2$ (incompletely); in the presence of ammonium salts there is no precipitation. As in the case of $Mg(OH)_2$, the cause is the relatively high solubility product of $Fe(OH)_2$ ($SP = 4.8 \times 10^{-16}$), which is not reached at

* The question of the "strength" of oxidizing and reducing agents will be discussed in more detail in Sections 61-64.

the OH^- concentration existing in mixtures of ammonia and ammonium salts. However, on standing the products of oxidation of $Fe(OH)_2$ by atmospheric oxygen are gradually precipitated.

3. Carbonates of the alkali metals and ammonium carbonate form a white precipitate of $FeCO_3$ with Fe^{++}; this turns brown rapidly in air owing to oxidation to $Fe(OH)_3$:

$$4FeCO_3 + 6H_2O + O_2 \rightleftarrows \downarrow 4Fe(OH)_3 + 4CO_2\uparrow$$

4. Potassium ferricyanide*, $K_3[Fe(CN)_6]$, forms a blue precipitate of Turnbull's blue with Fe^{++}:

$$3Fe^{++} + 2[Fe(CN)_6]^{---} = \downarrow Fe_3[Fe(CN)_6]_2$$

The precipitate is insoluble in acids but is decomposed by alkalies. This is the most characteristic reaction of the Fe^{++} ion**.

5. Dimethylglyoxime (Chugaev's reagent)*** forms red internally complex salts, soluble in water, with Fe^{++}. The reaction is carried out in ammoniacal solution in the presence of tartaric acid, added to form complexes with Fe^{+++} ions which would otherwise form a precipitate of $Fe(OH)_3$ with ammonia.

As dimethylglyoxime is an important reagent for Ni^{++}, with which it gives a pink precipitate, the presence of Fe^{++} interferes with detection of Ni^{++}. The test can be used for detection of Fe^{++} only in the known absence of Ni^{++} (or after nickel has been converted into the stable complex $[Ni(CN)_4]^{--}$ by the action of KCN).

6. Oxidation of Fe^{++} to Fe^{+++}. While Fe^{+++} is a weak oxidizing agent, Fe^{++} is a reducing agent which can be oxidized by a number of oxidizing agents, such as $KMnO_4$, $K_2Cr_2O_7$ in acid solution, HNO_3, etc. Let us examine the oxidation by nitric acid in detail. The equation is

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO\uparrow$$

or

$$3Fe^{++} + 4H^+ + NO_3^- = 3Fe^{+++} + 2H_2O + NO\uparrow$$

Acidify a solution of a ferrous salt with $2N$ H_2SO_4, add about 1 ml of concentrated nitric acid and heat until the brown colour disappears. The brown colour is due to the formation of the unstable complex compound $[Fe(NO)]SO_4$ which decomposes on heating.

---

* A salt of ferricyanic acid, $H_3[Fe(CN)_6]$, in which iron is trivalent. Do not confuse this reagent with $K_4[Fe(CN)_6]$, used for detection of Fe^{+++}.

** $K_3[Fe(CN)_6]$ does not give a precipitate with Fe^{+++} but the solution turns dark brown. $K_4[Fe(CN)_6]$ forms a white precipitate of $Fe_2[Fe(CN)_6]$ with Fe^{++}; this turns blue in air owing to oxidation of the iron and formation of Prussian blue.

*** The structural formula of dimethylglyoxime is given on p. 237.

The same reaction takes place when ferrous sulphide is dissolved in nitric acid:

$$FeS + 4HNO_3 = Fe(NO_3)_3 + \downarrow S + 2H_2O + NO\uparrow$$

or

$$FeS + 4H^+ + NO_3^- = Fe^{+++} + \downarrow S + 2H_2O + NO\uparrow$$

Therefore after separation of Group III cations from Groups II and I iron must be present as Fe^{+++} in the solution. This is convenient for analysis, because the precipitation of Fe^{+++} is more complete than that of Fe^{++}.

Ferrous iron can also be oxidized to ferric by hydrogen peroxide in either acid or alkaline solution. The reaction in alkaline solution is

$$2Fe^{++} + H_2O_2 + 4OH^- = \downarrow 2Fe(OH)_3$$

56. Reactions of the Mn^{++} Cation

Solutions of manganese salts are pale pink. Dilute solutions are colourless.

1. **Caustic alkalies, NaOH and KOH,** form a white precipitate of $Mn(OH)_2$ with Mn^{++}; this is soluble in acids but not in alkalies:

$$Mn^{++} + 2OH^- = \downarrow Mn(OH)_2$$

The precipitate quickly turns brown in air owing to oxidation; a compound of quadrivalent manganese, $MnO(OH)_2$ (or H_2MnO_3), is formed. If an oxidizing agent (hydrogen peroxide or bromine water) is added to a solution of a manganous salt together with an alkali, $MnO(OH)_2$ is formed at once as a dark brown precipitate:

$$Mn^{++} + H_2O_2 + 2OH^- = \downarrow MnO(OH)_2 + H_2O$$

In contrast to $Mn(OH)_2$, the $MnO(OH)_2$ precipitate is insoluble in dilute H_2SO_4. However, if 1-2 drops of H_2O_2 solution are also added and the liquid is heated, the precipitate dissolves (try this). Under these conditions (in acid solution) H_2O_2 reduces Mn^{IV} and is itself oxidized to free oxygen*:

$$MnO(OH)_2 + H_2O_2 + 2H^+ = Mn^{++} + 3H_2O + O_2\uparrow$$

It is also possible to reduce manganese (IV) to the bivalent state when $MnO(OH)_2$ is dissolved in H_2SO_4 by addition of a nitrite

---

* The electron transfer scheme here is

$$O_2^{--} - 2e = O_2$$

$$Mn^{+IV} + 2e = Mn^{++}$$

($NaNO_2$ or KNO_2), which becomes oxidized to nitrate ($NaNO_3$ or KNO_3). In contrast to sulphuric acid, hydrochloric acid dissolves $MnO(OH)_2$ (on heating); in this case the reduction is effected by Cl^- ions, which are oxidized to Cl_2:

$$MnO(OH)_2 + 4HCl = MnCl_2 + 3H_2O + Cl_2\uparrow$$

2. **Ammonia, NH_4OH,** like caustic alkalies, precipitates the Mn^{++} ion. However, the precipitation is incomplete owing to formation of NH_4^+ ions in the reaction:

$$Mn^{++} + 2NH_4OH \rightleftarrows \downarrow Mn(OH)_2 + 2NH_4^+$$

As a result, the pH of the solution falls below 10.3 (the value needed for complete precipitation of manganese hydroxide). If enough NH_4Cl is added, the pH is lowered so much that $Mn(OH)_2$ is not precipitated at all. It will be remembered that the reactions in the cases of $Mg(OH)_2$ and $Fe(OH)_2$ are similar. The action of a mixture of ammonia and an ammonium salt on the Mn^{++} ion is used to separate Mn^{++} from Al^{+++}, Cr^{+++} and Fe^{+++}, which are precipitated almost completely by such a mixture in the form of $Al(OH)_3$, $Cr(OH)_3$ and $Fe(OH)_3$. However, this separation is not sharp, because in ammoniacal solution Mn^{++} is gradually oxidized by atmospheric oxygen to quadrivalent manganese, which is precipitated as $MnO(OH)_2$.

3. **Carbonates of the alkali metals and ammonium carbonate** form a white precipitate of $MnCO_3$, soluble in acids.

4. **Disodium hydrogen phosphate, Na_2HPO_4,** precipitates white $Mn_3(PO_4)_2$, which is soluble in mineral acids and in *acetic acid* (distinction from Al^{+++}, Cr^{+++} and Fe^{+++}).

5. **The oxidation of Mn^{++} to MnO_4^-,** important for detection of the Mn^{++} ion, may be effected by various agents. Let us consider the following methods.

(a) *Oxidation by lead dioxide*, PbO_2. Put a small amount of PbO_2 powder (or Pb_3O_4) into a test tube, add HNO_3 (sp. gr. 1.2) and carefully heat to boiling, shaking the tube gently all the time (*the liquid may spurt out*). Let the PbO_2 settle and see whether the solution has turned pinkish. If so, the reagents contain manganese and cannot be used for this experiment. In the absence of any colour, add a *very small amount* (one drop) of the solution to be tested for Mn^{++}, free from Cl^- ions, such as $MnSO_4$ or $Mn(NO_3)_2$, mix, and heat again. The Mn^{++} ion is oxidized to permanganic acid, $HMnO_4$, which has a characteristic purple-violet colour*:

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O$$

* If the colour is very faint, add 1-2 more drops of the manganese salt solution and heat again.

or

$$2Mn^{++} + 5PbO_2 + 4H^+ = 2MnO_4^- + 5Pb^{++} + 2H_2O$$

The above equation shows that the oxidizing agent in this case is PbO_2, or, more correctly, quadrivalent lead, which is reduced to the bivalent state.

In this and the next reaction *a very small amount of the manganese (II) must be added*, because an excess reduces* the MnO_4^- ion formed to $MnO(OH)_2$:

$$2MnO_4^- + 3Mn^{++} + 7H_2O = 5MnO(OH)_2 + 4H^+$$

To confirm this experimentally, add 1-2 ml more of a solution of manganese (II) to the purple solution and heat again. Does the colour persist? For the same reason, *the solution must be free of all other reducing agents, and in particular of* Cl^- *ions*, as the latter also reduce MnO_4^- to $MnO(OH)_2$ or even to Mn^{++}:

$$2MnO_4^- + 16H^+ + 10Cl^- = 2Mn^{++} + 8H_2O + 5Cl_2\uparrow$$

(b) *Oxidation by ammonium persulphate*, $(NH_4)_2S_2O_8$, is effected in the presence of a catalyst, Ag^+ ions: the reaction is**

$$2MnSO_4 + 5(NH_4)_2S_2O_8 + 8H_2O = 2HMnO_4 + 5(NH_4)_2SO_4 + 7H_2SO_4$$

or

$$2Mn^{++} + 5S_2O_8^{--} + 8H_2O = 2MnO_4^- + 10SO_4^{--} + 16H^+$$

In the absence of Ag^+, or if an excess of Mn^{++} ions is present, brown $MnO(OH)_2$ is precipitated instead of MnO_4^-.

To carry out this reaction, add a little 2 *N* H_2SO_4 (or HNO_3) to 1-2 ml of $(NH_4)_2S_2O_8$ solution, followed by a few drops of a silver salt solution, and warm. Introduce the *smallest possible amount* (see above) of the solution to be tested for Mn^{++}, free from Cl^- ions, into the heated oxidizing mixture and mix the liquid. If the purple colour is too faint, a little more of the manganese solution may be added. On the other hand, if brown $MnO(OH)_2$ is precipitated this means that the Mn^{++} ion concentration is too high***. In that case repeat the experiment after diluting the manganese solution several-fold with water.

Since Cr^{+++} is also oxidized by $(NH_4)_2S_2O_8$, to give $Cr_2O_7^{--}$ (p. 271), this reaction can be used for detection of Cr^{+++} together with Mn^{++}. Having carried out the test for Mn^{++} as described above, add about

---

* The electron transfer scheme is

$$\begin{array}{rl} Mn^{++} - 2e = Mn^{+IV} & \mid 3 \\ Mn^{+VII} + 3e = Mn^{+IV} & \mid 2 \end{array}$$

** See the second footnote on p. 271.

*** Provided that no reducing agents are present in the solution.

1 ml more of the unknown solution into the same test tube and heat again. Filter off the precipitated $MnO(OH)_2$, *cool the filtrate*, and test it for $Cr_2O_7^{--}$ by conversion into H_2CrO_6 (p. 274).

(c) *Oxidation by sodium bismuthate**, $NaBiO_3$, is represented by the equation

$$2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 = 2HMnO_4 + 5Bi(NO_3)_3 + 5NaNO_3 + 7H_2O$$

or

$$2Mn^{++} + 5NaBiO_3 + 14H^+ = 2MnO_4^- + 5Bi^{+++} + 5Na^+ + 7H_2O$$

In contrast to the reactions studied above, this one proceeds in the cold; therefore excess of manganese (II) salts and small amounts of chlorides do not interfere. No other reducing agents must be present.

To carry out the test, take 1-2 ml of cold dilute HNO_3 in a test tube and add a few drops of a solution of a manganese (II) salt and a small amount of $NaBiO_3$ powder. Mix, allow the excess reagent to settle, and observe the purple colour of the solution.

Permanganic acid, $HMnO_4$, which is formed in these reactions is one of the strongest oxidizing agents. It can oxidize many different reducing agents. In acid solution Mn^{VII} is reduced to Mn^{II}, i.e., to Mn^{++} cations. In permanganate oxidations in alkaline or neutral solutions Mn^{VII} is reduced only to Mn^{IV}, which is precipitated as brown $MnO(OH)_2$.

Study some of the oxidation reactions of the MnO_4^- ion experimentally. To a solution of a ferrous salt acidified with H_2SO_4 add dilute potassium permanganate solution drop by drop and note the disappearance of its colour. The equation is

$$5Fe^{++} + MnO_4^- + 8H^+ = 5Fe^{+++} + Mn^{++} + 4H_2O$$

$KMnO_4$ is also decolourized when it is added to nearly boiling solutions of oxalic acid or its salts, acidified with H_2SO_4**:

$$5C_2O_4^{--} + 2MnO_4^- + 16H^+ = 2Mn^{++} + 10CO_2\uparrow + 8H_2O$$

Both these reactions are used in quantitative analysis.

Hydrogen peroxide, H_2O_2, which acts as a reducing agent in this case, can also be used for the reduction of MnO_4^- ions to Mn^{++} cations. The equation is

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{++} + 5O_2\uparrow + 8H_2O$$

The derivation of this equation is given on p. 250, 5.

---

* The reagent is prepared by fusion of a bismuth salt with sodium peroxide. As in the reaction with PbO_2, the purity of the reagents must be checked by means of a suitable "blank" experiment.

** See p. 248 for the derivation of the equation for this reaction.

6. Benzidine*, $C_{12}H_8(NH_2)_2$, is oxidized by manganese (IV) compounds with formation of blue products. The reaction is conveniently carried out by the drop method.

Put a drop of a solution of a manganese (II) salt on a strip of filter paper and treat with ammonia fumes. The $Mn(OH)_2$ formed is rapidly oxidized by atmospheric oxygen to $MnO(OH)_2$ and the spot turns brown. A drop of benzidine acetate applied to this spot is oxidized by $MnO(OH)_2$ and the spot becomes blue** (compare the corresponding reaction of CrO_4^{--}). The test will detect 0.15 μg of Mn^{++}. The dilution limit is 1 : 330,000.

In the presence of large amounts of Co^{++} a faint blue colour may appear in the absence of Mn^{++}. To avoid this, a drop of ammonium chloride solution should be applied to the spot on the paper before treatment with ammonia.

Silver chloride, AgCl, is reduced by Mn^{++} ions to metallic silver. This can also be performed as a spot test.

Put a drop of HCl solution on a strip of paper. Touch the centre of the damp spot with a capillary containing a silver salt solution. A precipitate of AgCl forms on the paper. Wash the precipitate thoroughly by putting in the middle of the spot a capillary containing as much water as it can hold by capillary forces. Keep it there until the spot has grown to 2-3 times its original size***. Now moisten the washed precipitate with a drop of the solution to be tested for Mn^{++} and add a small drop of concentrated NaOH. In the presence of Mn^{++}, which reduces AgCl to metallic silver, the spot turns black****

$$2AgCl + Mn^{++} + 4OH^- = \downarrow 2Ag + \downarrow MnO(OH)_2 + 2Cl^- + H_2O$$

---

* The structural formula of benzidine is given on p. 273.

** The reaction between $MnO(OH)_2$ and benzidine can be represented by the following equations:

$$C_{12}H_8(NH_2)_2 + MnO(OH)_2 + 2CH_3COOH = C_{12}H_8(NH)_2 + Mn(CH_3COO)_2 + 3H_2O$$

$$C_{12}H_8(NH)_2 + C_{12}H_8(NH_2)_2 = C_{12}H_8(NH)_2 - C_{12}H_8(NH_2)_2$$

At the first stage the $-NH_2$ (amino) groups of benzidine are oxidized to imino groups, $=NH$, by the action of $MnO(OH)_2$. At the second stage a molecule of the product, $C_{12}H_8(NH)_2$, combines with another molecule of benzidine to form a blue compound.

*** This operation may be repeated if necessary.

**** This test was proposed by N. A. Tananaev and I. V. Tananaev. It is more convenient to use ammoniacal $AgNO_3$ solution as the reagent. It is prepared as follows. Concentrated ammonia is added to saturated $AgNO_3$ solution until the precipitate redissolves. This is followed by addition of as much ammonia as has already been added. When this reagent is available for detection of Mn^{++}, a drop of the unknown solution and a drop of the reagent are applied one after the other to a strip of filter paper.

8. Microcrystalloscopic Test. Characteristic crystals of $MnC_2O_4 \cdot 3H_2O$ (Fig. 31) are formed when a crystal of oxalic acid is introduced into a solution of a manganous salt. The detectable minimum is 1 μg of Mn^{++}. Cations which form precipitates with oxalic acid (such as Zn^{++}, Ca^{++}, Ba^{++}, etc.), mineral acids, and large amounts of alkali-metal salts interfere with this reaction.

9. Dry-Way Test. *a. Bead Formation.* Make a bead of Na_2CO_3 in the loop of a platinum wire by the method used for making borax or sodium phosphate beads (p. 269). Pick up a little of the solid substance to be tested for manganese, such as $MnSO_4$ or $MnO(OH)_2$

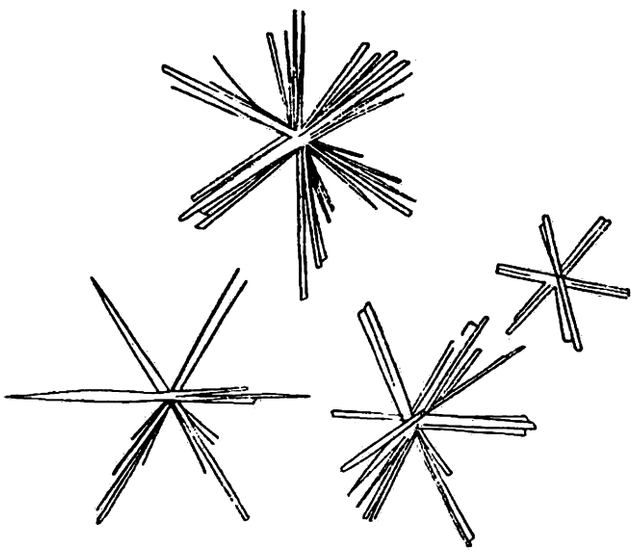


Fig. 31. Crystals of $MnC_2O_4 \cdot 3H_2O$

precipitate, on the bead and heat strongly. Now pick up a few $KClO_3$ crystals on the bead and heat cautiously again. A green (or light blue) bead indicates the presence of manganese. In the case of $MnO(OH)_2$ the equation is

$$3MnO(OH)_2 + 3Na_2CO_3 + KClO_3 =$$
$$= 3Na_2MnO_4 + KCl + 3H_2O \uparrow + 3CO_2 \uparrow$$

The manganese compound Na_2MnO_4 formed is a salt of manganic acid, H_2MnO_4, containing sexivalent manganese; it is a green salt and the colour of the bead is due to it.

b. Grinding Method (Method of F. M. Flavitsky). A small portion of the solid is ground with one or two crystals of $AgNO_3$ and a few crystals of Na_2CO_3. In the presence of manganese the reaction mixture turns black after 2-3 minutes owing to the reduction of $AgNO_3$ by manganese (II) to metallic silver.

To speed up the test, Na_2CO_3 may be omitted; the substance is then ground with one or two small crystals of $AgNO_3$ and treated

with a drop of NH_4OH solution. The mixture blackens instantaneously. The equation is

$$MnSO_4 + 2AgNO_3 + 4NH_4OH =$$
$$= \downarrow 2Ag + \downarrow MnO(OH)_2 + (NH_4)_2SO_4 + 2NH_4NO_3 + H_2O$$

57. Reactions of the Zn^{++} Cation

The Zn^{++} ion is colourless.

1. **Caustic alkalies, NaOH and KOH,** give a white precipitate of $Zn(OH)_2$ with Zn^{++} ions. It is soluble in both acids and alkalies (amphoterism), e.g.:

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$
$$\underset{(H_2ZnO_2)}{Zn(OH)_2} + 2NaOH = Na_2ZnO_2 + 2H_2O$$

Na_2ZnO_2 is sodium zincate.

The ionic equations for the reactions are

$$Zn(OH)_2 + 2H^+ = Zn^{++} + 2H_2O$$
$$H_2ZnO_2 + 2OH^- = ZnO_2^{--} + 2H_2O$$

In contrast to aluminates, zincates do not form a precipitate of $Zn(OH)_2$ with NH_4Cl, because zinc hydroxide is soluble in ammonium salts (see below).

2. **Ammonia, NH_4OH,** also precipitates $Zn(OH)_2$, which dissolves in excess NH_4OH (and in ammonium salts) owing to the formation of complex zinc ammine ions $[Zn(NH_3)_6]^{++}$, for example:

$$Zn(OH)_2 + 6NH_4OH = [Zn(NH_3)_6](OH)_2 + 6H_2O$$

Therefore the Zn^{++} ion is not precipitated by NH_4OH in the presence of ammonium salts.

3. **Carbonates of the alkali metals and ammonium carbonate** form white precipitates of variable composition, soluble in acids.

4. **Disodium hydrogen phosphate, Na_2HPO_4,** gives a white precipitate of $Zn_3(PO_4)_2$, soluble in acids and ammonia. In the presence of ammonium salts the less soluble salt $ZnNH_4PO_4$ is precipitated (compare Mg^{++}).

5. **Hydrogen sulphide, H_2S,** precipitates Zn^{++} in the form of white ZnS:

$$Zn^{++} + H_2S \rightleftarrows \downarrow ZnS + 2H^+$$

The behaviour of the Zn^{++} ion with H_2S distinguishes it from all the other Group III cations, which are not precipitated by hydrogen sulphides, and is similar to the behaviour of Group IV cations.

The reason for the precipitation of Zn^{++} is that the solubility product of ZnS is considerably smaller than those of the other Group III sulphides. Calculations and experiments show that the precipitation of Zn^{++} is almost complete even in acid solutions if the pH is not below 2.

By treatment with H_2S at pH = 2, Zn^{++} can be detected in the presence of the other Group III cations (and also Groups II and I).

Only the Fe^{+++} ion interferes with this reaction, because it oxidizes H_2S to free sulphur in the form of a white precipitate similar to ZnS. Of course, the solution must not contain any other oxidizing agents such as MnO_4^- or $Cr_2O_7^{--}$ ions, hydrogen peroxide, etc.

In systematic analysis of cations, Group III is analyzed after precipitation of cations of Groups IV and V by hydrogen sulphide in acid solution (at pH = 0.5). At this stage Fe^{+++} becomes reduced to Fe^{++}, which does not interfere with detection of Zn^{++}. If the pH of the solution after separation of Groups IV and V is raised from 0.5 to 2 (i.e., if the H^+ ion concentration is lowered from 0.3 to 0.01 g-ion/litre) and H_2S is then passed through it, the formation of a white precipitate of ZnS, soluble in acids, indicates the presence of Zn^{++}. The simplest way of adjusting the pH to 2 is to add formate buffer mixture, HCOOH + $HCOONH_4$, i.e., a mixture of free formic acid and a formate in suitable concentrations.

If Groups IV and V are absent it is more convenient to remove interfering Fe^{+++} ions by shaking the solution with $CaCO_3$ powder. This neutralizes the acids present in the solution and raises the pH to about 5. Since $Fe(OH)_3$ is completely precipitated even at pH = 3.5 (see Table 10, p. 128), Fe^{+++} ions are removed. $Al(OH)_3$ and (partially) $Cr(OH)_3$ are precipitated together with $Fe(OH)_3$. On the other hand, Zn^{++} ions remain completely in the solution, because precipitation of $Zn(OH)_2$ begins only at pH = 6.5. It must be remembered that the reaction with $CaCO_3$ must be conducted in the cold, because the hydrolysis of this salt is intensified so much by heating that $Zn(OH)_2$ may also be precipitated.

After removal of the precipitated hydroxides and excess $CaCO_3$, the filtrate is tested for Zn^{++} by the action of hydrogen sulphide at pH = 2. The pH may be adjusted to this value not only by addition of formate buffer mixture to the almost neutral solution obtained as described above, but also by addition of *exactly* 1/4 of its volume of 0.05 *N* HCl. This lowers the concentration of the HCl solution 5-fold, to 0.01 *N*, and the pH of such a solution is 2.

The method for fractional detection of Zn^{++} by this reaction is given in the description of Group III analysis (p. 303). If it is performed carefully, the results are quite reliable.

6. **Potassium ferrocyanide, $K_4[Fe(CN)_6]$,** gives a white precipitate of the double ferrocyanide of potassium and zinc with Zn^{++}; this

is soluble in alkalies:

$$3ZnSO_4 + 2K_4[Fe(CN)_6] = \downarrow K_2Zn_3[Fe(CN)_6]_2 + 3K_2SO_4$$

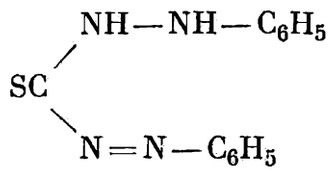
$$3Zn^{++} + 2K^+ + 2[Fe(CN)_6]^{=\!=} = \downarrow K_2Zn_3[Fe(CN)_6]_2$$

This reaction distinguishes Zn^{++} from Al^{+++}, which does not form a precipitate with $K_4[Fe(CN)_6]$.

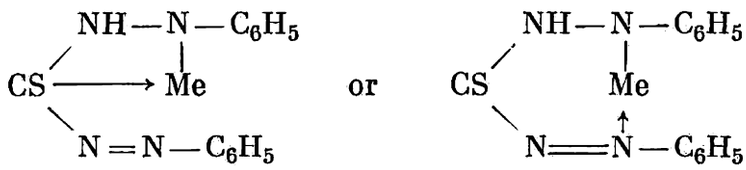
7. Potassium ferricyanide, $K_3[Fe(CN)_6]$, gives a brownish yellow precipitate of zinc ferricyanide, $Zn_3[Fe(CN)_6]_2$, soluble in HCl and NH_4OH, with Zn^{++}.

8. Dithizone*, used in the form of a solution in chloroform ($CHCl_3$) or in carbon tetrachloride (CCl_4), forms a crimson-red internally complex salt with Zn^{++}; in distinction from analogous compounds (dithizonates) of other elements, in alkaline solutions this salt colours the aqueous layer as well as the layer of $CHCl_3$ or CCl_4. The reaction is used for fractional detection of Zn^{++} in the presence of other cations, including all the Group III cations. The most convenient procedure is as follows. Treat three drops of the unknown solution in a small crucible (or on a watch glass) with a small amount of solid sodium peroxide, Na_2O_2. When the violent reaction is over, transfer a drop of the solution, which may contain ZnO_2^{--}, AlO_2^- and CrO_4^{--} ions with excess NaOH, together with the precipitated hydroxides to a strip of paper by means of a capillary. Do not take the tip of the capillary off the paper until a watery zone several millimetres wide has formed around the precipitate. Now draw a ring around the damp spot with a capillary containing dithizone solution. A characteristic crimson ring indicates the presence of Zn^{++}. If Zn^{++} is absent an orange ring is formed, characteristic of dithizone in alkaline solution. To distinguish the colours with certainty, put a drop of 2 *N* NaOH on the paper by the side of the spot and act on it with a drop of dithizone solution**. It is convenient

* The shortened name of diphenylthiocarbazone



This reagent forms coloured internally complex salts with many heavy metals; the following structures have been ascribed to them:



** This method of carrying out the test was devised by L. M. Orlova.

to combine this test with the benzidine spot test for chromium, described on p. 273.

9. Action of $(NH_4)_2[Hg(CNS)_4]$* in the presence of $CoCl_2$. Take about 1 ml of *very dilute* $CoCl_2$ solution (not stronger than 0.02%) and add an equal volume of $(NH_4)_2[Hg(CNS)_4]$. Rub the walls of the test tube for half a minute with a glass rod and confirm that no blue precipitate is formed. Then add 1-2 drops of a zinc salt solution and again rub with a glass rod for not more than half a minute. A blue or azure precipitate containing $Co[Hg(CNS)_4]$ and $Zn[Hg(CNS)_4]$ forms rapidly. The equations are:

$$CoCl_2 + (NH_4)_2[Hg(CNS)_4] = \downarrow Co[Hg(CNS)_4] + 2NH_4Cl$$

$$ZnSO_4 + (NH_4)_2[Hg(CNS)_4] = \downarrow Zn[Hg(CNS)_4] + (NH_4)_2SO_4$$

The white precipitate of $Zn[Hg(CNS)_4]$ formed by the zinc ion accelerates (by seeding) the formation of the blue $Co[Hg(CNS)_4]$ precipitate, which may not form for hours in the absence of $Zn[Hg(CNS)_4]$ (formation of a supersaturated solution). Mixed crystals of the two compounds are formed, coloured pale or dark blue in accordance with the amount of Zn^{++}. It should be remembered that $Co[Hg(CNS)_4]$ *is precipitated rapidly from more highly concentrated cobalt salts even in the absence of* Zn^{++}. Therefore $CoCl_2$ solutions stronger than 0.02% must not be used.

It is also evident that the presence of considerable amounts of Co^{++} in the solution interfere with the test. Ni^{++} and Fe^{++} ions, which form greenish precipitates with $(NH_4)_2[Hg(CNS)_4]$, also interfere. In the presence of Fe^{+++} a violet precipitate may be formed. Moreover, the colour of the precipitate may be masked by the formation of the intensely coloured ferric thiocyanate, $Fe(CNS)_3$. To avoid these complications, NaF or NH_4F may be added to convert Fe^{+++} into the $[FeF_6]^{---}$ complex (p. 276, 4).

It must also be borne in mind that the test cannot be carried out in a strongly acid solution because the $Zn[Hg(CNS)_4]$ precipitate is soluble in concentrated acids. The precipitate, like the reagent $(NH_4)_2[Hg(CNS)_4]$, is decomposed by alkalies with formation of a yellow precipitate of HgO. Therefore the test must be carried out in a weakly or moderately acid solution (the acid concentration must not exceed 0.5 *N*).

10. Reaction with Methyl Violet. The action of the organic dye methyl violet on a neutral or very slightly acid solution of a zinc salt in the presence of NH_4CNS yields a suspension of minute salt crystals formed by the organic dye cation and the complex $[Zn(CNS)_4]^{--}$ anion; the suspension has a violet colour by transmitted light.

* This reagent is known as ammonium tetrathiocyanatomercurate.

It is best to carry out this test as follows. To 2 ml of water add 5 drops of saturated tartaric acid solution*, 1 drop of HCl (sp. gr. 1.12), 2 drops of 20% NH_4CNS solution, and 1 drop of 0.06% methyl violet solution**. The solution acquires a bluish-green colour (due to the presence of H^+ ions). Divide it into two portions; leave one for comparison and to the other add 1-2 drops of the solution to be tested for Zn^{++} and shake the tube. A change of the colour to violet (or blue at low zinc concentrations) indicates the presence of Zn^{++}.

Excess of acid is detrimental to the test; therefore acid solutions must be neutralized as exactly as possible before testing.

All the directions regarding the amounts and concentrations of the reagents used must also be followed exactly, otherwise the result of the test may be wrong.

Of the Group III cations the only interfering ion is Fe^{+++}, which gives a blood-red colour with NH_4CNS (p. 276). To detect Zn^{++} in the presence of Fe^{+++}, treat about 1 ml of the unknown solution with excess NH_4OH and NH_4Cl. This precipitates Fe^{+++} as $Fe(OH)_3$ while Zn^{++} forms the complex $[Zn(NH_3)_6]^{++}$, which remains in solution. Filter off the precipitate and acidify the filtrate slightly with HCl (to decompose the complex); then test the filtrate for Zn^{++} as described above.

It is also possible to reduce Fe^{+++} to Fe^{++} by heating with metallic lead, but this method is less reliable than the one just described.

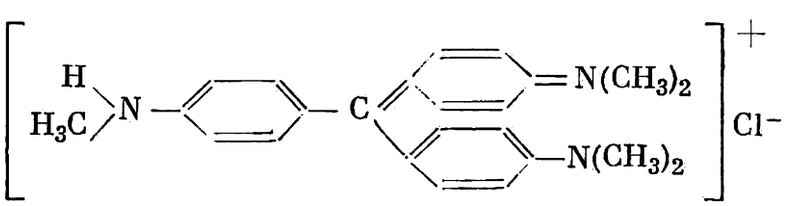
11. Microcrystalloscopic Test. To a drop of a zinc salt solution acidified with CH_3COOH add a drop of $(NH_4)_2[Hg(CNS)_4]$ on a glass slide and examine the $Zn[Hg(CNS)_4]$ crystals under the microscope. They appear as characteristic crosses and dendrites (Fig. 32,*a*).

The crystals deposited from dilute zinc salt solutions, or solutions acidified with mineral acids, are in the shape of irregular triangles and wedges (Fig. 32,*b*). Such solutions should first be evaporated, a drop being placed on a glass slide. The dry residue is cooled and treated with a drop of the reagent.

---

* To form complexes with certain interfering cations.

** Methyl violet is a chloride of an organic base, and has the structure



Violet ink, which is usually made from this dye, can be used as the reagent. The concentration of the ink solution must be chosen so that after addition of 1 drop of HCl (sp. gr. 1.12) and 1 drop of ink to 2 ml of water the solution is turned violet (in the absence of Zn^{++}) by 3-4 drops but not by 2 drops of 20% NH_4CNS solution. If violet colour is produced by 2 drops, the ink solution is too concentrated and must be diluted with water.

The test detects 0.1 μg of Zn^{++}. The dilution limit is 1 : 10,000.

12. Dry-Way Test. Moisten a small strip of filter paper with a solution of a zinc salt and *dilute* $Co(NO_3)_2$ solution. Dry and burn the

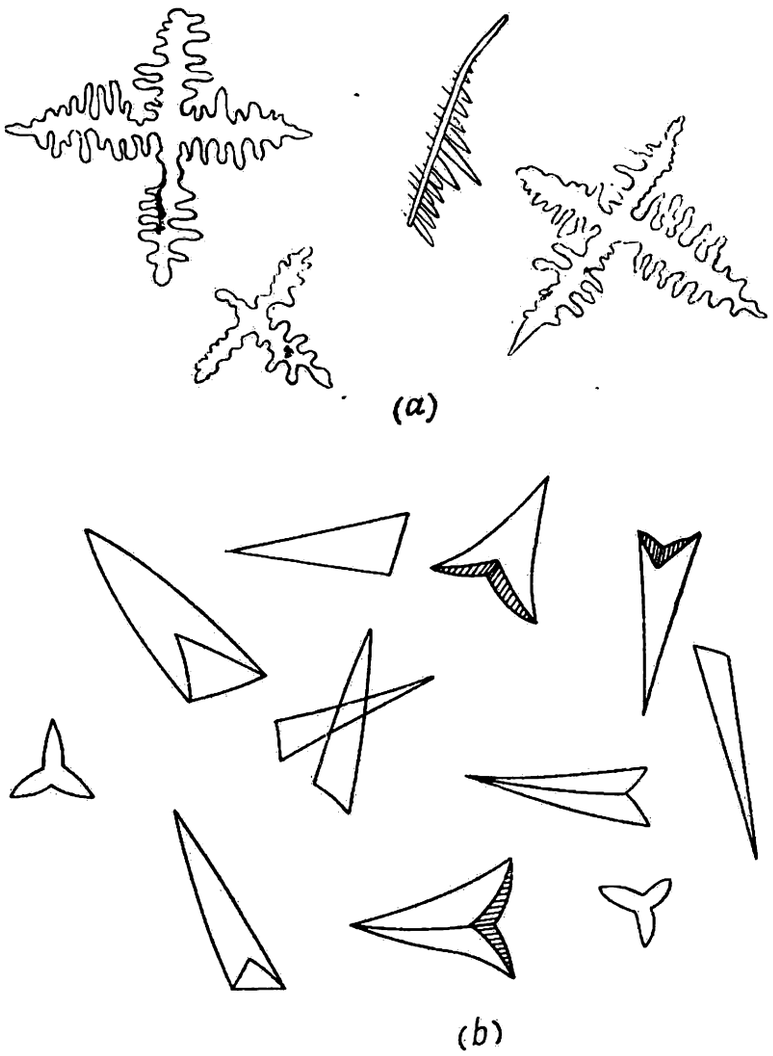


Fig. 32. Crystals of $Zn[Hg(CNS)_4]$

paper. The ash is found to be green owing to the formation of cobalt zincate (Rinmann's green). The equation is

$$Zn(NO_3)_2 + Co(NO_3)_2 = CoZnO_2 + 4NO_2 \uparrow + O_2 \uparrow$$

58. Reactions of the Co^{++} Cation

Anhydrous cobalt salts are blue. Crystalline hydrates and dilute solutions of cobalt salts are pink. This colour is due to hydrated $[Co(OH_2)_6]^{++}$ ions. Evaporation of the solutions or the action of dehydrating agents such as alcohol, concentrated HCl, etc., changes the colour from pink to blue owing to dehydration of the complex

ions and replacement of H_2O molecules by other ligands; for example:

$$\underset{\text{Pink}}{[Co(OH_2)_6]Cl_2} \longrightarrow \underset{\text{Blue}}{[Co(OH_2)_4Cl_2]} + 2H_2O$$

1. Caustic alkalies, NaOH and KOH, precipitate the blue basic salts with Co^{++} ions:

$$Co^{++} + Cl^- + OH^- = \downarrow Co\begin{matrix}OH\\Cl\end{matrix}$$

On further addition of alkali and heating the precipitate is converted into pink cobalt (II) hydroxide:

$$CoOHCl + OH^- = \downarrow Co(OH)_2 + Cl^-$$

The $Co(OH)_2$ precipitate gradually turns brown in air, being converted into cobalt (III) hydroxide:

$$4Co(OH)_2 + O_2 + 2H_2O = 4Co(OH)_3$$

The action of an alkali and hydrogen peroxide on a solution of a cobalt salt immediately produces a dark brown precipitate of $Co(OH)_3$:

$$2Co^{++} + 4OH^- + H_2O_2 = \downarrow 2Co(OH)_3$$

The precipitate is insoluble in H_2SO_4, but dissolves in mixtures of sulphuric acid with H_2O_2 or $NaNO_2$, which reduce Co^{III} to Co^{II} in acid solution (compare Mn).

2. Ammonia, NH_4OH, also precipitates the blue basic salt, which dissolves in the presence of a large excess of NH_4OH or ammonium salts to give a complex compound of a dingy yellow colour*:

$$CoOHCl + 7NH_4OH = [Co(NH_3)_6](OH)_2 + NH_4Cl + 6H_2O$$

In the presence of ammonium salts, ammonia does not precipitate the Co^{++} ion. However, if Fe^{+++}, Al^{+++} or Cr^{+++} are present, Co^{++} is partially coprecipitated with them.

3. Carbonates of the alkali metals form reddish precipitates of basic salts of variable composition, soluble in dilute acids, ammonia, and ammonium carbonate.

4. Disodium hydrogen phosphate, Na_2HPO_4, gives a violet precipitate of $Co_3(PO_4)_2$ soluble in acids.

5. Ammonium thiocyanate, NH_4CNS, forms the complex salt $(NH_4)_2[Co(CNS)_4]$ with Co^{++} ions:

$$Co^{++} + 2NH_4^+ + 4CNS^- = (NH_4)_2[Co(CNS)_4]$$

* On standing in air the solution gradually turns red owing to the formation of the trivalent cobalt complex $[Co(NH_3)_6]^{+++}$. An ammine complex of cobalt (III) is also formed by the action of a mixture of NH_4OH and H_2O_2 on a solution of a cobalt (II) salt.

If amyl alcohol (or a mixture of amyl alcohol with ether) is added to the solution and shaken, the complex is extracted by the solvent (being more soluble in these solvents than in water) and colours the solvent layer blue. In carrying out this most characteristic test for Co^{++} it should be remembered that the $[Co(CNS)_4]^{--}$ complex is not very stable ($K_{inst} = 1 \times 10^{-3}$). Therefore, to make the test work, the dissociation of this complex into Co^{++} and CNS^- ions must be suppressed by the introduction of a large excess of thiocyanate. Take 2-3 ml of saturated NH_4CNS (it is even better to add a small amount of the solid salt) and 1-2 ml of amyl alcohol per ~0.5 ml of the cobalt (II) salt solution. The Fe^{+++} ion interferes, as it gives a blood-red colour with NH_4CNS, masking the colour due to Co^{++}. Therefore the Fe^{+++} ion is converted into the $[FeF_6]^{---}$ complex by addition of NH_4F or NaF solution until the red colour disappears (p. 276).

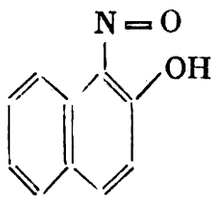
The sensitivity of the test can be raised by the following procedure. Put 1-2 drops of the weakly acidic unknown solution (together with a few milligrams of solid fluoride if Fe^{+++} is present) on a spot plate, add 5 drops of saturated NH_4CNS solution in acetone, and mix. The colour of the solution becomes blue or green, dependent on the amount of Co^{++} present.

Finally, this test is very conveniently carried out as a spot test on a strip of *newspaper*. This type of paper contains lignin, in the presence of which the cobalt thiocyanate complex is more stable and is not decomposed by water. It is best to use newspaper previously impregnated with saturated NH_4CNS and NH_4F solutions and dried. A drop of the solution under test forms a blue spot on this paper. If Fe^{+++} is also present, a brown colour appears first, due to the formation of $Fe(CNS)_3$, but this gradually fades as the Fe^{+++} ions are removed by the F^- ions, and the blue colour of the cobalt thiocyanate complex takes its place.

6. Il'insky's reagent. Cobalt (II) in bivalent cobalt salts is oxidized to cobalt (III) by α-nitroso-β-naphthol. A bulky red-brown precipitate of an internally complex salt is formed*. To carry out the test, add a few drops of the reagent to about 1 ml of a neutral or weakly

---

* The formula of α-nitroso-β-naphthol is



The compound formed by α-nitroso-β-naphthol with cobalt has the formula $[C_{10}H_6(NO)O]_3Co$.

acidic cobaltous salt (CH_3COONa should be added to strongly acidic solutions) and heat.

Fe^{+++}, which forms a brownish black precipitate with the reagent, interferes.

7. **Ammonium tetrathiocyanatomercurate, $(NH_4)_2[Hg(CNS)_4]$,** gives a blue precipitate of $Co[Hg(CNS)_4]$ with the Co^{++} ion (Sec. 57, 9). A small amount of a zinc salt hastens the precipitation and the colour is then pale blue. The precipitate dissolves in concentrated HCl to form a blue solution which turns pink when diluted with water. Caustic alkalies and ammonia decompose the reagent and precipitate yellow mercuric oxide. The precipitate is almost insoluble in dilute hydrochloric acid.

8. **Potassium nitrite, KNO_2,** added in excess to a moderately dilute solution of a cobalt (II) salt acidified with acetic acid, forms a yellow crystalline precipitate of the complex salt $K_3[Co(NO_2)_6]$:

$$Co^{++} + 7NO_2^- + 3K^+ + 2CH_3COOH =$$
$$= \downarrow K_3[Co(NO_2)_6] + NO \uparrow + 2CH_3COO^- + H_2O$$

This test can be used for distinguishing and separating Co^{++} and Ni^{++}. In dilute solutions the precipitate appears after warming and standing.

9. **Microcrystalloscopic Test.** The formation of bright blue $Co[Hg(CNS)_4]$ crystals, described above, can be used for microscopic detection of Co^{++} (Fig. 33).

Evaporate a drop of a neutral or weakly acidic solution of a cobalt (II) salt to dryness on a glass slide, cool, and add a drop of the reagent. Leave for some time if necessary. In the presence of Fe^{+++} a small grain of NaF should be introduced into the drop before addition of the reagent.

10. **Dry-Way Tests.** *a. Borax bead formation.* Cobalt compounds form blue beads with borax, $Na_2B_4O_7 \cdot 10H_2O$ (see p. 269, 5). *Large* amounts of Ni^{++}, which gives a brown bead, interfere.

b. Grinding method (method of F. M. Flavitsky). Grind a few crystals of the solid under test with a few crystals of NH_4CNS in a porcelain basin (or on a porcelain tile) with the narrow end of a pestle. If the mixture turns brown (indicating the presence of Fe^{III}; see p. 277, 8) grind it with a few crystals of $Na_2S_2O_3$. This reduces ferric iron to ferrous and the $Fe(CNS)_3$ colour disappears. If cobalt is present, this colour is replaced by the dark (or light) blue colour due to $(NH_4)_2[Co(CNS)_4]$. If the blue product is treated with a drop of water, the cobalt complex decomposes to give Co^{++} and CNS^- ions and the blue colour changes to pink. Thus, water interferes with this reaction and if it is carried out in the wet way (see above, 5), the reaction product must be extracted in an organic solvent (amyl alcohol) which is immiscible with water. Extraction is not required

if the grinding method is used. The reaction is more sensitive by this method than in solution.

It is interesting to note that a number of other reactions which do not occur in the presence of water can be effected by the grinding method. For example, Co^{II} can be detected if the solid is ground

Fig. 33. Crystals of $Co[Hg(CNS)_4]$

with $Na_2S_2O_3$; a blue colour appears owing to the formation of a cobalt thiosulphate complex. This reaction does not occur in aqueous solutions.

59. Reactions of the Ni^{++} Cation

The Ni^{++} ion is green in aqueous solutions.

1. Caustic alkalies, NaOH and KOH, form a green precipitate of $Ni(OH)_2$ with the Ni^{++} ion:

$$Ni^{++} + 2OH^- = \downarrow Ni(OH)_2$$

The precipitate is soluble in acids.

2. Ammonia, NH_4OH, first gives a green precipitate of a basic salt, $(NiOH_2)SO_4$, which then dissolves in excess NH_4OH to form

a blue complex salt. The equation is

$$NiSO_4 + 6NH_4OH = [Ni(NH_3)_6]SO_4 + 6H_2O$$

or

$$Ni^{++} + 6NH_4OH = [Ni(NH_3)_6]^{++} + 6H_2O$$

Ammonia does not precipitate the Ni^{++} ion in the presence of ammonium salt, owing to the formation of the complex cation $[Ni(NH_3)_6]^{++}$.

3. Carbonates of the alkali metals form a green precipitate of nickel carbonate, $NiCO_3$, which is soluble in acids and in ammonia and ammonium carbonate solutions.

4. Disodium hydrogen phosphate. Na_2HPO_4, gives a green precipitate of $Ni_3(PO_4)_2$, which is soluble in acids (including acetic acid). The precipitate also dissolves in ammonia but not in caustic alkalies.

5. Dimethylglyoxime (Chugaev's reagent) forms a characteristic bright red precipitate of an internally complex salt with the Ni^{++} ion in ammoniacal solution. The equation is given on p. 237.

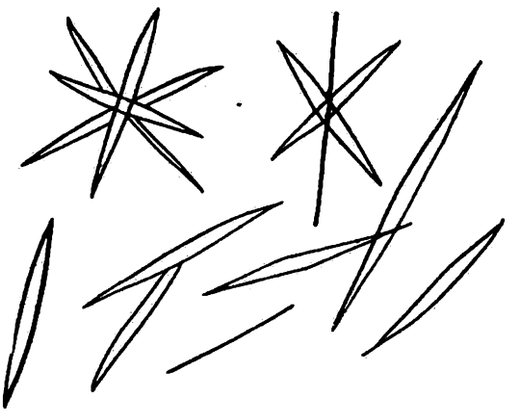


Fig. 34. Crystals of nickel dimethylglyoximate

To carry out the test, add a drop of dimethylglyoxime solution and a drop of dilute ammonia to the drop of a solution of a nickel salt, and examine the precipitate of nickel dimethylglyoximate.

Foremost among the conditions for carrying out this most important test for Ni^{++} is the influence of the solution pH.

The test fails if the solution is considerably acid, because dimethylglyoxime is a weak acid and the complex formed by it is decomposed by H^+ ions (p. 234). Excess of ammonia should also be avoided. as this favours the formation of a nickel ammine complex. In general, the pH range for fairly complete precipitation of Ni^{++} by dimethylglyoxime is between 5 and 10. The reaction may be effected in the presence of acetate buffer mixture (CH_3COOH with excess CH_3COONa) at pH $\approx$ 5.

Fe^{++} ions *interfere with this reaction*, as they give a red colour with dimethylglyoxime (see p. 278, 5) owing to the formation of a soluble internally complex salt (try this). Cations such as Fe^{+++}, which form coloured insoluble hydroxides with NH_4OH must also be absent, as they may mask the colour.

It is possible to detect Ni^{++} in the presence of interfering ions by carrying out the test on paper with Na_2HPO_4. Put a drop of Na_2HPO_4 solution on a strip of paper, touch the middle of the damp

spot with a capillary containing the unknown solution, and add another drop of Na_2HPO_4 solution. Now draw a capillary containing dimethylglyoxime solution around the spot and treat the spot with ammonia vapour. A pink ring forms in the presence of Ni^{++}; the whole spot becomes pink in the presence of large amounts.

The function of the Na_2HPO_4 is to form sparingly soluble phosphates such as $FePO_4$ with interfering cations, and these then remain in the middle of the spot. The more soluble nickel phosphate is situated at the edges of the spot and is detected there.

6. **Microcrystalloscopic Test.** Dimethylglyoxime can also be used for detection of Ni^{++} by this method. Add a drop of ammonia and a drop of dimethylglyoxime solution (or a small crystal of the solid reagent). Viewed under the microscope, the precipitate is seen as red needles, often in clusters (Fig. 34). The detectable minimum is 0.2 μg Ni^{++}. Cobalt salts (at high concentrations), and copper and ferrous salts interfere.

60. Analysis of Mixtures of Group III Cations

The most important reactions of the Group III cations are summarized in Table 17.

The chemical changes we have met in our study of Group III cations are more diverse and complex than those of Groups II and I. Therefore several different methods can be devised for analysis of Group III. These methods differ, in the first instance, in the way the Group III cations are initially divided into subgroups.

The ammonia method of separation into subgroups is based on the action of NH_4OH in the presence of ammonium salts; Al^{+++}, Cr^{+++} and Fe^{+++} are precipitated as hydroxides while the cations Mn^{++}, $[Zn(NH_3)_6]^{++}$, $[Co(NH_3)_6]^{++}$ and $[Ni(NH_3)_6]^{++}$ remain in solution. Instead of ammonia, the organic base *pyridine*, C_5H_5N, may be used in the presence of an ammonium salt to give pH = 6.5; the hydroxides of aluminium, iron (III) and chromium (III) are precipitated while the other Group III cations remain in solution as soluble complex salts of pyridine (see p. 258).

In the *alkali method* separation into subgroups is effected by the action of excess NaOH at the boil; Al^{+++} and Zn^{++} are converted into aluminate (AlO_2^-) and zincate (ZnO_2^{--}) ions and remain in solution, while the other Group III cations are precipitated as hydroxides*.

In the *hydrogen peroxide method* excess alkali in the presence of hydrogen peroxide (or sodium peroxide) is used for separation

* In the cold, chromium is also dissolved in the form of chromite. Chromites are hydrolyzed on heating and $Cr(OH)_3$ is precipitated (Sec. 54, 1).

into subgroups. This treatment converts Al^{+++} and Zn^{++} cations into AlO_2^- and ZnO_2^{--} anions, which remain in solution together with the CrO_4^{--} ions formed by oxidation of CrO_2^- by hydrogen peroxide. The remaining cations are precipitated as $Fe(OH)_3$, $MnO(OH)_2$, $Co(OH)_3$ and $Ni(OH)_2$.

In the *acetate method* (suitable only in the absence of chromium) the solution is boiled with CH_3COONa to precipitate Al^{+++} and Fe^{+++} as the basic acetates $CH_3COO(OH)_2Al$ and $CH_3COO(OH)_2Fe$, while the other cations remain in solution.

When the above methods are used, Co^{++} and Ni^{++} are usually separated first; the separation is based on the fact that CoS and NiS are insoluble in dilute HCl, while the other Group III sulphides dissolve. The separation of Co^{++} and Ni^{++} is incomplete, as usually they partially dissolve when the precipitated sulphides are treated with HCl. However, this does not lead to analytical errors and may be disregarded.

It must be pointed out, however, that all the other methods for separating the Group III cations are greatly complicated by coprecipitation effects (Sec. 42) and are therefore far from perfect. For example, in the ammonia method Co^{++} is appreciably coprecipitated, and Mn^{++} partially, with the hydroxides of aluminium, chromium and iron. Therefore it is better to detect them before separation of the subgroups, before they have become distributed between the precipitate and the solution. In the hydrogen peroxide method (and especially in the alkali method) Zn^{++} is coprecipitated considerably with the precipitate ions and is often "missed" in systematic analysis. To avoid this, Zn^{++} should be detected by the fractional method, before precipitation of Group III cations by ammonium sulphide. The zinc ion can be tested for either by the reaction with H_2S in the presence of formate buffer mixture or 0.01 *N* HCl, or by the dithizone reaction.

Analysis of mixtures of Groups III, II and I cations by the hydrogen peroxide (p. 302), ammonia (p. 310) and pyridine (p. 312) methods is described below. The first two methods are illustrated by schemes (Tables 18 and 19) which are not analytical instructions but merely represent the sequence of the operations and the resulting separations of ions.

It must be remembered that all these analytical procedures are applicable only in the absence of PO_4^{---}. See Sec. 113 for the procedure when phosphate is present in the unknown solution.

Whereas the cations of Groups II and I, studied earlier, are colourless and form white precipitates in most cases, in Group III we often have to deal with coloured ions (Cr^{+++}, Ni^{++}, Co^{++}, Fe^{+++}) and precipitates. *The colours of both are very important analytical characteristics* which merit the most serious attention. Sometimes

Reagents	Cations		
	Al^{+++}	Cr^{+++}	Fe^{+++}
$(NH_4)_2S$	White ppt. **$Al(OH)_3$**	Grey-green or grey-violet ppt. **$Cr(OH)_3$**	Black ppt. **Fe_2S_3**
H_2S in presence of HCOOH and $HCOONH_4$	—	—	Reduction to Fe^{++}, S ppt.
NaOH or KOH	$Al(OH)_3$	$Cr(OH)_3$	Brown ppt. **$Fe(OH)_3$**
KOH or NaOH in excess on boiling	**No ppt.** (AlO_2^- formed)	$Cr(OH)_3$	$Fe(OH)_3$
KOH or NaOH in excess in presence of H_2O_2 on boiling	**No ppt.** (AlO_2^- formed)	**No ppt.** (CrO_4^{--} formed, solution yellow)	$Fe(OH)_3$
NH_4OH	$Al(OH)_3$	$Cr(OH)_3$	$Fe(OH)_3$
NH_4OH, excess in presence of ammonium salts	**$Al(OH)_3$**	**$Cr(OH)_3$**	**$Fe(OH)_3$**
CH_3COONa on boiling	White ppt. $CH_3COO(OH)_2Al$	No ppt. ***	Brown ppt. $CH_3COO(OH)_2Fe$
Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$	$Al(OH)_3$	$Cr(OH)_3$	$Fe(OH)_3$

Table 17

III Cations

Cations				
Fe++	Mn++	Zn++	Co++	Ni++
Black ppt. **FeS**	Flesh-coloured ppt. **MnS**	White ppt. **ZnS**	Black ppt. **CoS**	Black ppt. **NiS**
—	—	**ZnS**	—	—
Greenish ppt. turning brown $Fe(OH)_2$	White ppt. turning brown $Mn(OH)_2$	White ppt. $Zn(OH)_2$	Blue ppt. of basic salts	Greenish ppt. $Ni(OH)_2$
$Fe(OH)_2$	$Mn(OH)_2$	**No ppt.** (ZnO_2^{--} formed)	Pink ppt. $Co(OH)_2$	$Ni(OH)_2$
Brown ppt. **$Fe(OH)_3$**	Brown ppt. **$MnO(OH)_2$**	**No ppt.** (ZnO_2^{--} formed)	Dark brown ppt. $Co(OH)_3$	$Ni(OH)_2$
$Fe(OH)_2$	$Mn(OH)_2$	$Zn(OH)_2$	Basic salts	Basic salts
— *	— *	— **	— **	— **
—	—	—	—	—
White ppt. turning brown	White ppt. $MnCO_3$	Basic salts	Basic salts	Green ppt. $NiCO_3$

Reagents	Cations		
	Al^{+++}	Cr^{+++}	Fe^{+++}
Na_2HPO_4	White ppt. **** $AlPO_4$	Green ppt. $CrPO_4$	Yellowish ppt.**** $FePO_4$
$K_4[Fe(CN)_6]$	**No ppt.**	—	Blue ppt. $Fe_4[Fe(CN)_6]_3$
$K_3[Fe(CN)_6]$	—	—	—
Oxidizing agents	—	Formation of yellow (CrO_4^{--}) or orange ($Cr_2O_7^{--}$) solution	—
Borax or $NaNH_4HPO_4$ bead	—	**Emerald green**	—

* Oxidation products, $Fe(OH)_3$ or $MnO(OH)_2$, gradually precipitated.
** Complex ions $[Zn(NH_3)_6]^{++}$, $[Co(NH_3)_6]^{++}$, $[Ni(NH_3)_6]^{++}$ formed.
*** Cr^{+++} partially precipitated in the presence of Al^{+++} and Fe^{+++}.
**** $AlPO_4$ and $FePO_4$ precipitates are insoluble in CH_3COOH. All the other phosphates are soluble in acetic acid.

this makes analysis much easier and the results are more reliable. For example, if an unknown solution is colourless it cannot contain any considerable amounts of the coloured ions mentioned above.

Similarly, if a white precipitate is formed with $(NH_4)_2S$ it may be concluded that the unknown solution does not contain Fe^{+++}, Fe^{++}, Ni^{++} or Co^{++} ions, as their sulphides are black. If the colour of the precipitate is pure white, the presence of Al^{+++} or Zn^{++} is to be expected; Cr^{+++} is probably present if the precipitate is grey-green, and Mn^{++} if it is pink. Of course, different ions present together may mask each other's colours, but often such masking does not occur. Observation of colours makes analysis much easier. On the other hand, errors are often revealed if the colours of the solutions or precipitates are taken into consideration. For example, if

Continued

Cations				
Fe^{++}	Mn^{++}	Zn^{++}	Co^{++}	Ni^{++}
White ppt. $Fe_3(PO_4)_2$	White ppt. $Mn_3(PO_4)_2$	White ppt. $Zn_3(PO_4)_2$	Violet ppt. $Co_3(PO_4)_2$	Green ppt. $Ni_3(PO_4)_2$
White ppt. $Fe_2[Fe(CN)_6]$	White ppt.	White ppt. $K_2Zn_3[Fe(CN)_6]_2$	Green ppt.	Pale green ppt.
Blue ppt. $Fe_3[Fe(CN)_6]_2$	Brown ppt.	Yellow ppt.	Dark red ppt.	Yellow-brown ppt.
Fe^{+++}	Purple violet solution (MnO_4^-) or brown ppt. $MnO(OH)_2$	—	Dark brown ppt. $Co(OH)_3$	Black ppt. $Ni(OH)_3$
Brown or greenish	Violet or amethyst	—	**Blue**	Brown

Fe^{+++}, Fe^{++}, Co^{++} and Ni^{++} are not found during analysis of Group III but the sulphide precipitate is black, it is obvious that some kind of error was made. This example shows the importance of noting the colours both of the unknown solution and of the precipitates formed during analysis.

Valuable indications of the probable presence or absence of certain cations in solution are also sometimes given by pH determinations. For example, if a solution is strongly alkaline (pH >10) and does not smell of ammonia, it cannot contain any cations which do not form amphoteric hydroxides. Therefore in such cases only aluminium, cromium and zinc of the Group III cations need be tested for, as these are present in alkaline solutions in the form of AlO_2^-, CrO_2^- (or CrO_4^{--}) and ZnO_2^{--} anions. If the alkalinity of the solution is due to the presence of ammonia, or ammonia with an ammonium salt, it may contain Fe^{++}, Mn^{++}, $[Zn(NH_3)_6]^{++}$,

$[Ni(NH_3)_6]^{++}$ and $[Co(NH_3)_6]^{++}$, but Fe^{+++}, Al^{+++} or Cr^{+++} (if the pH does not exceed 10) cannot be present.

If the solution is acid, it may contain any of the Group III cations; but even in this case the pH may be significant. For example, if the pH $\geqslant$ 5, it is very likely that Fe^{+++} is absent, because it is precipitated completely as $Fe(OH)_3$ even at pH = 3.5 (Table 10, p. 128). Similarly, at pH = 5-6 the presence of Al^{+++} is unlikely, because it is completely precipitated* at pH = 5.1. However, *such conclusions must be regarded as preliminary*, and must be confirmed by subsequent tests. It must be remembered that pH values are determined only to the nearest unit and that the situation is considerably complicated by the simultaneous presence of several cations, which makes conclusions more difficult to draw. Nevertheless, determinations of the solution pH and observations of the colour are very useful, as they provide certain indications. In conjunction with the analytical results they support the validity of the analysis, especially in the case of chemically individual substances.

It must not be forgotten that the acid reaction of a solution may depend not only on the presence of particular Group III cations but also on the presence of free acids which are often added deliberately during analysis, as in the precipitation of Groups IV and V by hydrogen sulphide, in the separation of Group II sulphates, etc. Obviously, direct determinations of pH are pointless in such cases. In order to obtain a pH value which might serve as some kind of analytical indication of the cations present, the free acids must first be neutralized until a turbidity appears which persists on stirring. The best stage for pH determination during analysis is after the solution has been neutralized before precipitation of Group III cations by ammonium sulphide (see below, p. 304, 3).

ANALYSIS OF A MIXTURE OF GROUPS III, II, AND I

Hydrogen peroxide method

1. Dissolving the Precipitate and Separating Group II Sulphates.** If the solution contains a precipitate, test its solubility in dilute (2 *N*) HCl, using a separate portion of the liquid with the precipitate stirred up in it.

(a) If the precipitate dissolves in HCl, dissolve it (in the whole of the unknown solution) in the minimum amount of HCl. Investigate the solution as described in 2.

---

* Solutions of ferrous and ferric salts and of certain aluminium salts (for example, $AlCl_3$) are acidified to suppress hydrolysis, so that they are strongly acidic.

** In the absence of a precipitate, proceed as indicated in 2.

(b) If the precipitate does not dissolve when tested as described, add several millilitres of 2 *N* HCl to the whole solution in order to dissolve all the acid-soluble components (carbonates, hydroxides, etc.) and heat the solution to boiling. Filter off the undissolved residue of Group II sulphates, wash it, and investigate as described on p. 173. Investigate the filtrate as indicated in 2.

2. Preliminary Observations and Tests. *a. Note the colour of the solution*; draw inferences concerning the presence or absence of coloured cations (see above).

b. Determination of the solution pH. If the solution had been acidified at the previous stages of the analysis, the pH is determined after neutralization of the solution until a slight turbidity appears (and persists on stirring), before precipitation of Group III cations by ammonium sulphide (see 3). This should also be done when the pH determination shows that the solution is strongly acidic (pH $<<2$), indicating the presence of free acids.

c. Test for NH_4^+. Ammonium ions are introduced into the solution in precipitation of Group III cations by the group reagent, and therefore ammonium must be tested for by the fractional method previously. The test is performed in the usual way, either by the action of excess NaOH or with Nessler's reagent. In the latter case a separate portion of the solution must be taken, Group III cations precipitated in it by alkali, and NH_4^+ tested for in the filtrate (p. 286).

d. Tests for Fe^{+++} *and* Fe^{++} must be carried out before the precipitation of Group III, because after the Group III precipitate has been dissolved in HNO_3 all the iron is present in the form of Fe^{++} ions.

The Fe^{+++} *Ion.* Mix 1 drop each of the unknown solution, 2 *N* HCl, and $K_4[Fe(CN)_6]$ solution on a spot plate. A blue precipitate of Prussian blue, $Fe_4[Fe(CN)_6]_3$, proves the presence of Fe^{+++}. Another drop of the acidified solution may be tested with a drop of NH_4CNS solution; a red colour is obtained owing to formation of $Fe(CNS)_3$.

Fe^{++} is detected by the action of $K_3[Fe(CN)_6]$ on a separate portion of the acidified solution. A blue precipitate of Turnbull's blue $Fe_3[Fe(CN)_6]_2$, indicates the presence of Fe^{++}.

Since $K_3[Fe(CN)_6]$ gives coloured precipitates with several other Group III cations in addition to Fe^{++} (see Table 17), the precipitate formed with Fe^{++} may be dark green rather than blue if other cations are present.

e. Zinc can be detected by the reaction with H_2S in the presence of formate buffer (p. 285). However, if Fe^{+++} is present it oxidizes hydrogen sulphide to sulphur, which is precipitated as a white powder resembling ZnS. To avoid confusion, proceed as follows. To 1 ml of the unknown solution add Na_2CO_3 solution drop by drop

until a permanent turbidity forms. Dissolve this in 1-2 drops of 2 *N* hydrochloric acid, and continue adding the acid until about 1/5 of the volume of the original solution (*not more*) has been added*. Now pass hydrogen sulphide through the solution for about 2 minutes (*in the fume cupboard*). Filter off any white precipitate of sulphur. Add an equal volume of formate buffer to the filtrate immediately, and pass H_2S again. The formation of a white precipitate of ZnS, soluble in excess HCl, indicates the presence of Zn^{++}. If no precipitate forms, continue to pass hydrogen sulphide for 2-3 minutes more; only then can the absence of zinc be assumed.

The following method can also be used for detecting Zn^{++}. Take about 1 ml of the filtrate after separation of Group II sulphates and of Groups IV and V cations**, dilute it three-fold with water, add one drop of methyl orange indicator and neutralize with ammonia until a permanent turbidity forms, or until the indicator turns yellow (if there is no turbidity). Now remove excess ammonia by adding 2 *N* HCl drop by drop until the turbidity disappears and the colour changes to red. Cool*** the slightly acid solution and add solid $CaCO_3$ until some remains undissolved after vigorous shaking. This neutralizes the excess HCl and hydrolysis of $CaCO_3$ makes the solution slightly alkaline; the alkalinity is sufficient to precipitate the least soluble hydroxides, and in particular $Fe(OH)_3$, but not the much more soluble zinc hydroxide. Filter off and reject the precipitate, containing excess $CaCO_3$, $Fe(OH)_3$ and other hydroxides. Add 0.05 *N* HCl to the filtrate (which should be yellow) drop by drop until one drop changes the colour to red. Now add more 0.05 *N* HCl, the amount added being *exactly* one-quarter of the volume of the filtrate. The HCl concentration is then exactly 0.01 *N*, and the pH is adjusted to the required value of 2 for precipitation of zinc sulphide. Heat the solution and pass H_2S through it. If Zn^{++} is present, white ZnS is precipitated; the precipitate dissolves when concentrated hydrochloric acid is added drop by drop.

This method gives very reliable results if the instructions are followed exactly.

3. Separation of Group III Cations from Groups II and I**.** Group III cations form precipitates with Na_2HPO_4, $(NH_4)_2CO_3$, $(NH_4)_2C_2O_4$

---

* It is essential to keep strictly to the instructions concerning the preliminary neutralization and subsequent acidification with hydrochloric acid, because the composition of the formate buffer is such that the solution pH is 2 only under the specified conditions. If too much acid is added, ZnS is not precipitated. Conversely, if there is not enough acid, zinc sulphide may be precipitated together with sulphur during the first treatment with H_2S.

** The presence of Fe^{++} is undesirable in this method, because it is not precipitated by $CaCO_3$ and, remaining in solution, may be partially oxidized by atmospheric oxygen to Fe^{+++}. Therefore any Fe^{++} present must be oxidized to Fe^{+++} by boiling the solution with 2-3 drops of HNO_3 (sp. gr. 1.2). Cool the solution and proceed as described.

*** The treatment with $CaCO_3$ must be performed in the cold, because hydrolysis of $CaCO_3$ is intensified on heating and the solution becomes so alkaline that Zn^{++} may be precipitated.

**** Before this separation is carried out with the whole solution, find whether Group III is present by carrying out the test with a portion of the solution in a test tube. If Group III is absent, proceed as described on p. 173.

and other reagents used in analysis of Groups II and I; therefore Group III must be separated from the other two groups.

The separation is performed as follows. Add a small amount of NH_4Cl to the solution and neutralize the excess acid, as otherwise Group III sulphides will not be precipitated (Sec. 52). Add 2 *N* ammonia *slowly* to the solution until a faint permanent turbidity* due to hydroxides appears (or, in the absence of turbidity**, until the solution is weakly alkaline).

Now heat the solution nearly to boiling and add (*in a fume cupboard*) about 1/3 of its own volume of ammonium sulphide solution***.

Test for complete precipitation and add more $(NH_4)_2S$ if necessary. When the precipitation is complete, leave the contents of the flask to stand for at least half an hour (to convert NiS and CoS into forms less soluble in HCl; see p. 261). Then filter off the precipitate and wash it with water containing a little NH_4Cl (to prevent formation of colloidal sulphides) and $(NH_4)_2S$ (to prevent oxidation of sulphides to sulphates by atmospheric oxygen). *Immediately* destroy excess ammonium sulphide in the filtrate as described in 11. Investigate the precipitate as indicated in 4.

The filtrate from Group III should be colourless, or yellowish owing to the presence of excess ammonium sulphide. A dark or reddish colour indicates the formation of colloidal sulphides of Group III. In that case coagulate them by adding NH_4Cl or CH_3COONH_4 and boiling. Filter off the precipitate and add it to the main precipitate.

4. **Separation of Co^{++} and Ni^{++}.** Take the filter paper from the funnel, open it out, transfer the precipitated Group III sulphides and hydroxides into a porcelain basin with the aid of a glass rod, and treat the precipitate immediately (*in a fume cupboard*) in the cold with 1 *N* HCl (2 *N* HCl diluted with an equal volume of water).

Stir the contents of the basin with a glass rod for about 5 minutes, filter off the undissolved CoS and NiS, wash the residue with hot water containing NH_4Cl, and investigate as directed in 5. Investigate the filtrate as indicated in 6.

5. **Detection of Co^{++} and Ni^{++}.** Transfer the precipitate of CoS and NiS to a beaker or porcelain basin and boil it with a mixture of 2 *N* HCl and H_2O_2. When the precipitate has dissolved, filter off

---

* An excess of ammonia favours the formation of colloidal solutions of sulphides. Therefore if too much ammonia has been added, and a precipitate rather than a turbidity has formed, dissolve the precipitate in the smallest possible amount of HCl and again add NH_4OH drop by drop.

** This may be the case if no Fe^{+++}, Al^{+++} or Cr^{+++} is present.

*** First confirm that the reagents, NH_4OH and $(NH_4)_2S$, do not form precipitates with $BaCl_2$, i.e., that they do not contain $(NH_4)_2CO_3$ or $(NH_4)_2SO_4$. Otherwise there is a risk of "losing" Group II.

the precipitated sulphur (which should be of a light or dark grey colour; if the residue is black, add more H_2O_2 and boil again). Test the solution as follows.

(a) *For cobalt* by the reaction with NH_4CNS in the presence of amyl alcohol. Take about 1-2 ml of *saturated* NH_4CNS solution in a test tube and add a small amount of amyl alcohol and *2-3 drops* of the solution to be tested. Shake the tube. A blue colour, due to the formation of $(NH_4)_2 \cdot [Co(CNS)_4]$, indicates the presence of Co^{++}. If the colour is red, indicating the formation* of $Fe(CNS)_3$, add NH_4F solution drop by drop with shaking to convert Fe^{+++} into the $[FeF_6]^{---}$ complex; the blue colour of the cobalt salt can then be seen.

It is also possible to use the Il'insky test (p. 292, 6), the reaction with $(NH_4)_2[Hg(CNS)_4]$ in the presence of 1-2 drops of a solution of a zinc salt (p. 293, 7), or the microcrystalloscopic test (p. 293, 9).

(b) *For nickel* by the Chugaev reaction in the presence of NH_4OH or CH_3COONH_4 (p. 295).

6. Separation of Fe^{++} and Mn^{++} from Al^{+++}, Cr^{+++} and Zn^{++}. Boil the filtrate obtained in 4, containing Al^{+++}, Cr^{+++}, Fe^{++}, Mn^{++} and Zn^{++} (Fe^{+++} is reduced by hydrogen sulphide when the sulphides are dissolved in HCl; see p. 262) together with excess HCl and H_2S, to remove hydrogen sulphide.

Now add concentrated (25%) NaOH until the solution is alkaline, followed by more NaOH (one quarter of the total volume of the solution), and a few millilitres of H_2O_2. After the vigorous reaction accompanied by evolution of oxygen has ceased, boil the liquid for a few minutes.

The caustic alkali first precipitates the hydroxides of all the cations present. However, on further addition of NaOH the amphoteric hydroxides of aluminium, chromium (III) and zinc dissolve in excess of alkali to form AlO_2^-, CrO_2^- and ZnO_2^{--} anions. Finally, on boiling with hydrogen peroxide CrO_2^- is oxidized to CrO_4^{--}, and the hydroxides of iron (II) and manganese (II) to $Fe(OH)_3$ and $MnO(OH)_2$. The latter are therefore found in the precipitate, while CrO_4^{--}, AlO_2^- and ZnO_2^{--} go into solution.

Filter off the precipitate and investigate it as described in 7. The filtrate is examined in accordance with 8.

7. Detection of Mn^{++} and Fe^{+++}. The precipitate must be *washed thoroughly* until Cl^- is removed completely (as it would interfere with detection of Mn^{++} by oxidizing it to $HMnO_4$)**. Continue the

---

* The solution may contain Fe^{+++} if the precipitate of CoS and NiS had not been washed thoroughly or if the hydrochloric acid used to dissolve it contained salts as an impurity.

** It is not essential to remove Cl^- completely if Mn^{++} is detected by the action of $NaBiO_3$ (p. 282).

washing until a few drops of the washings from the funnel, collected on a watch glass, no longer give (after acidification with HNO_3) a turbidity of Hg_2Cl_2 with a drop of $Hg_2(NO_3)_2$ solution.

Dissolve the washed precipitate by warming it with HNO_3 containing a small amount of KNO_2 or $NaNO_2$ (to reduce Mn^{IV} to Mn^{II}, as otherwise the $MnO(OH)_2$ precipitate would not dissolve in HNO_3). Boil the solution to decompose excess nitrite and test for Mn^{++} and Fe^{+++} in separate portions*.

(a) *Manganese.* Dilute a few drops of the solution with a small amount of water and add a little $NaBiO_3$. A purple or violet colour ($HMnO_4$) indicates the presence of Mn^{++} (p. 282, 5, *c*).

It is also possible to use the reactions with PbO_2 in the presence of HNO_3 or with $(NH_4)_2S_2O_8$ in the presence of $AgNO_3$ (as catalyst). It will be remembered that in both cases *a very small amount* of the unknown solution must be used, as otherwise a brown precipitate of $MnO(OH)_2$ is formed instead of $HMnO_4$. The best procedure is to moisten a glass rod with the diluted solution and to dip it for an instant into the heated oxidation mixture. If the purple colour is too weak, the operation should be repeated.

(b) *Iron* is detected by the tests with $K_4[Fe(CN)_6]$ or NH_4CNS (p. 276).

8. Detection of CrO_4^{--}. A yellow colour indicates the presence of CrO_4^{--} in the solution. Confirm this by the following tests.

(a) Put a drop of the solution on a strip of paper and add a drop of benzidine acetate solution. A blue colour confirms the presence of CrO_4^{--}.

(b) Acidify a few drops of the solution with acetic acid until it smells of the acid, and add a few drops of a lead salt solution. In the presence of CrO_4^{--} yellow** $PbCrO_4$ is precipitated.

If CrO_4^{--} is present, remove it as described in 9. In the absence of CrO_4^{--} proceed as in 10.

9. Separation of CrO_4^{--}. Add CH_3COOH to the solution *until it is acid* and precipitate CrO_4^{--} by $BaCl_2$ solution. Filter off the precipitated $BaCrO_4$ (and $BaSO_4$)***. Investigate the filtrate as described in 10. If the indications of the presence of CrO_4^{--} by the previous tests are doubtful, it may be confirmed at this stage. Treat the precipitate on heating with 1-2 ml of 2 *N* HCl or HNO_3; filter off and

---

* Of course, if the presence or absence of iron has been conclusively established by preliminary tests, there is no need to test for it at this stage.

** In the absence of CrO_4^{--} a white precipitate of $PbSO_4$ may form if the precipitate of Group III sulphides had not been washed free from SO_4^{--} ions present in the original solution.

*** $BaSO_4$ may be formed from SO_4^{--} ions adsorbed from the original solution by the precipitated Group III sulphides if these had not been washed thoroughly.

discard the residue. *Cool* the filtrate and add a little amyl alcohol and 1-2 drops of hydrogen peroxide. Mix the contents of the test tube at once. A blue ring of perchromic acid, H_2CrO_6, proves the presence of chromium.

10. Aluminium and zinc are detected in separate portions of the solution obtained in 9, or in 6 if CrO_4^{--} is absent. In the latter case CH_3COOH must be added to the solution until it is acid*.

(a) *Aluminium.* To a portion of the acid solution add solid NH_4Cl (to prevent precipitation of zinc hydroxide, which is soluble in ammonium salts; see p. 285) and NH_4OH until the liquid smells of ammonia. Boil the solution. A white flocculent precipitate of $Al(OH)_3$ indicates the presence of Al^{+++}. To confirm, filter off the precipitate, wash it, and dissolve it in the minimum amount of acetic acid. Carry out confirmatory tests for Al^{+++} with this solution; for example, the tests with aluminon, alizarin or morin (pp. 267-268).

Success in reliable detection of aluminium depends on correct acidification of the solution and subsequent addition of ammonia. If not enough acid is added, aluminium is present in the form of AlO_2^- anions, which are not precipitated by NH_4OH. On the other hand, if the amount of ammonia added is not sufficient the solution is acid and $Al(OH)_3$ is not precipitated. A large excess of NH_4OH is also undesirable, because the precipitate may dissolve to form aluminate. If the amount of Al^{+++} is small, the flakes of the precipitate are difficult to see and the contents of the flask or test tube must be examined very carefully; the flakes often float to the top.

(b) *Zinc.* Heat another portion of the solution acidified with acetic acid and pass H_2S through it. A white precipitate of ZnS, soluble in HCl, indicates the presence of Zn^{++}. To confirm, filter off the precipitate and dissolve it in the minimum amount of 2 *N* HCl. Evaporate a drop of the solution to dryness on a glass slide, cool the residue, treat it with $(NH_4)_2[Hg(CNS)_4]$ solution, and leave for 1-2 minutes. Characteristic crystals of $Zn[Hg(CNS)_4]$ (Fig. 32) confirm the presence of Zn^{++}.

Alternatively, Zn^{++} can be tested for with $(NH_4)_2[Hg(CNS)_4]$ in the presence of 0.02% $CoCl_2$ solution (*not stronger*—see p. 288, 9). Before this test boil out the H_2S formed when ZnS is dissolved in HCl. This method can also be used to detect Zn^{++} directly in a part of the filtrate from the separation of $BaCrO_4$, after acidification with 2 *N* HCl.

It will be remembered that the separation of Zn^{++} from Fe^{+++} and Mn^{++} as described in 6 is not sharp. A very large excess of alkali is needed for com-

* In order to avoid excessive dilution of the solution, the large excess of alkali present should be neutralized by concentrated acetic acid solution, added in small portions until a drop of the solution no longer produces a red colour on phenolphthalein paper (paper impregnated with 1% phenolphthalein solution and dried).

Table 18

Analysis of Mixtures of Groups III-I

(hydrogen peroxide method)

1. Dissolve ppt. in dilute HCl, separate insoluble residue of $BaSO_4$, $SrSO_4$ ($CaSO_4$). Investigate by Table 12

2. Preliminary tests with separate portions for (a) NH_4^+; (b) Fe^{++} and Fe^{+++}; (c) Zn^{++}

3. Precipitate Group III by $(NH_4)_2S$ in presence of NH_4OH and NH_4Cl

Precipitate: $Al(OH)_3$, $Cr(OH)_3$, Fe_2S_3, FeS, MnS, ZnS, CoS, NiS

Filtrate: Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, K^+, Na^+ [$(NH_4)_2S$, etc.]

4. Treat the ppt. with 1 *N* HCl in the cold to separate Co^{++} and Ni^{++}

Residue: CoS and NiS

Filtrate: Al^{+++}, Cr^{+++}, Fe^{++}, Mn^{++}, Zn^{++} [HCl, H_2S]

5. Dissolve at the boil in a mixture of HCl and H_2O_2. Separate precipitated sulphur. Test for Co^{++} and Ni^{++}

6. Separate Fe^{++} and Mn^{++} from Al^{+++}, Cr^{+++} and Zn^{++} by excess NaOH in presence of H_2O_2 at the boil

Ppt.: $Fe(OH)_3$, $MnO(OH)_2$

Filtrate: AlO_2^-, CrO_4^{--}, ZnO_2^{--} (NaOH)

7. Wash thoroughly, dissolve in HNO_3 in presence of KNO_2. Test for Mn^{++} and Fe^{+++}

8. Test for CrO_4^{--}

9. Separate CrO_4^{--} by action of $BaCl_2$ on solution acidified with CH_3COOH

Ppt.: $BaCrO_4$

Filtrate: Al^{+++}, Zn^{++} (CH_3COOH)

Not investigated

10. Test for Al^{+++} and Zn^{++} (in acid solution)

11. Decompose $(NH_4)_2S$ by boiling with CH_3COOH. Remove the precipitated sulphur. Remove most of the ammonium salts by evaporation and ignition. Dissolve the residue in HCl. Test for Group II and I cations by Table 12

plete separation of Zn^{++}; otherwise all the zinc may be in the precipitate. Therefore it may happen that zinc is not detected at this stage although it is found by preliminary tests.

11. Preparation of the Solution for Detection of Group I and II Cations. The solution obtained in 3, which contains cations of Groups I and II together with excess $(NH_4)_2S$ and other ammonium compounds must be boiled *immediately* (to avoid oxidation of S^{--} to SO_4^{--} by atmospheric oxygen) with excess CH_3COOH to remove ammonium sulphide. CH_3COONH_4 is formed and H_2S is evolved (*a fume cupboard must be used*). When the smell of hydrogen sulphide has disappeared, filter off the precipitated sulphur, and then remove most of the ammonium salts by evaporation and strong heating. This is essential, because in the presence of a large excess of ammonium salts the precipitation of Ba^{++}, Sr^{++} and Ca^{++} by ammonium carbonate is incomplete (or may not occur at all), as Group II carbonates are appreciably soluble in ammonium salts. Treat the dry residue with water acidified with HCl; filter the solution and analyze the filtrate for Groups II and I as described on pp. 172-173.

It may nevertheless happen that S^{--} ions are partially oxidized to SO_4^{--} during the analysis. In that case the residue after the heating contains Group II sulphates. Therefore if this residue does not dissolve in water acidified with HCl it must be tested for sulphates as indicated on p. 172.

The ammonia method

Analysis by the ammonia method involves the same initial stages as the above method with H_2O_2 (i.e., stages 1 to 3 in the above description). The subsequent procedure is described below.

4. Dissolving the Precipitated Group III Sulphides and Hydroxides, and Oxidation of Fe^{++} to Fe^{+++}. *Thoroughly wash* the precipitate of Group III sulphides and hydroxides obtained in 3 and treat it, on heating, with 6 *N* HNO_3 after addition of 3-5 drops of KNO_2 solution to accelerate the reaction. If a black residue remains after 2-3 minutes of heating, add more HNO_3 and heat again. Filter off and discard the precipitated sulphur*. Dilute the filtrate with water.

Nitric acid is used, because NiS and CoS do not dissolve in hydrochloric or sulphuric acid (p. 261). Moreover, HNO_3 oxidizes Fe^{++} to Fe^{+++}, and this is also an advantage in analysis. Investigate the filtrate according to 5.

5. Detection of Co^{++} and Mn^{++}. During the subsequent precipitation of the hydroxides of aluminium, chromium and ferric iron by ammonia in the presence of NH_4Cl there is considerable copre-

* It may be coloured grey or dark grey by traces of adsorbed sulphides. Any turbidity due to sulphur remaining after filtration may be disregarded.

cipitation of Co^{++} and Mn^{++}, and these ions become distributed between the precipitate and the filtrate. Therefore they should be tested for before the hydroxide precipitation. The tests are carried out on separate portions of the solution formed when the Group III sulphides and hydroxides have been dissolved in HNO_3 (as described in 4).

(a) *Cobalt* is detected by the same tests as in the previous method (see p. 305, 5) in a portion of the nitric acid solution.

(b) *Manganese.* Dilute 5 drops of the solution with 3-4 ml of water, and add 1 ml of 6 *N* HNO_3 and a small amount of powered $NaBiO_3$. Stir the liquid with a glass rod and allow excess $NaBiO_3$ to settle. A violet or pink colour in the solution (due to MnO_4^-) indicates the presence of Mn^{++}.

Other tests for Mn^{++} may also be used; for example, the tests with PbO_2 or $(NH_4)_2S_2O_8$ (see Sec. 56, 5). It must be remembered, however, that even small amounts of Cl^- ions reduce MnO_4^- to $MnO(OH)_2$ (brown precipitate) or even to Mn^{++}, and therefore interfere in these tests. The Group III precipitate adsorbs Cl^- ions, and appreciable amounts of chloride enter the solution when the precipitate is dissolved (especially if the washing of the precipitate had not been thorough). This has little interfering effect on the test for Mn^{++} with $NaBiO_3$, which is carried out in the cold; but for the other tests Cl^- ions must be removed. To do this, add 2 *N* NaOH to 2-4 ml of the solution, heat, filter, wash the precipitate twice, dissolve it in 4-6 drops of 2 *N* H_2SO_4, dilute with a few drops of water, and test the diluted solution for Mn^{++}. Remember that the tests with PbO_2 and $(NH_4)_2S_2O_8$ are effective only if very small amounts of Mn^{++} are present (p. 280).

It is also possible to remove Cl^- ions in the form of gaseous HCl. Evaporate to dryness 5-10 drops of the solution in a microcrucible with 5-10 drops of 2 *N* H_2SO_4. Cool the residue, dissolve it in a few drops of water, and test 5 drops of the solution for Mn^{++} by the above tests.

6. Precipitation of Al^{+++}, Cr^{+++} and Fe^{+++}. Add saturated NH_4Cl solution to the nitric acid solution containing the Group III cations (obtained as described in 4), heat, and add concentrated (13 *N*) NH_4OH solution to precipitate Al^{+++}, Cr^{+++} and Fe^{+++}. Add ammonia until the reaction is alkaline, after which 5 drops more should be added. Note the colour of the precipitate and draw appropriate inferences. Filter off the precipitate* and wash it once with water containing NH_4Cl.

During this operation the hydroxides of Al^{+++}, Cr^{+++} and Fe^{+++} are precipitated. The remaining Group III cations (the hydroxides of which are soluble in excess ammonia or in ammonium salts) are mainly present in solution as Mn^{++} ions, $[Zn(NH_3)_6]^{++}$, $[Ni(NH_3)_6]^{++}$ and $[Co(NH_3)_6]^{++}$. However, some Mn^{++} and Co^{++} may be precipi-

---

* If the filtrate is turbid, heat it again for several minutes on a water bath and filter it again. Combine the two precipitates and wash them.

tated as the hydroxides*. Investigate the precipitate according to 7 and the filtrate according to 9.

7. Separation of Fe^{+++} from Cr^{+++} and Al^{+++}. Treat the precipitate obtained in 6 with 6 *N* NaOH and heat. Continue the heating and add (in single drops) 5-6 drops of 3% H_2O_2, mixing the contents of the test tube for some time after each addition. Heat for 2-3 minutes and filter.

During this operation $Al(OH)_3$ dissolves in the alkali to form aluminate (AlO_2^- ions); $Cr(OH)_3$ forms CrO_4^{--} ions with alkali in the presence of H_2O_2. The residue therefore contains $Fe(OH)_3$ together with the previously coprecipitated hydroxides of manganese (II) and cobalt (II), which are oxidized by H_2O_2 to $MnO(OH)_2$ and $Co(OH)_3$. Since all the ions present in the residue were found earlier, it need not be investigated**.

The filtrate contains CrO_4^{--}, AlO_2^- and excess NaOH; it is analyzed according to 8.

8. Chromium and aluminium are detected in separate portions of the filtrate from *7*.

a. Test for CrO_4^{--} as described in the hydrogen peroxide method, 8 (p. 307).

b. Al^{+++} *Ions.* Without separating CrO_4^{--}, acidify the strongly alkaline solution with 2 *N* H_2SO_4 to pH $\ll 4$; then add ammonia until weakly alkaline (pH $\approx$ 9) and heat***. A white flocculent precipitate of $Al(OH)_3$ indicates the presence of Al^{+++}. In the presence of Al^{+++} filter off and wash the precipitate, dissolve it in acetic acid, and confirm the presence of Al^{+++} with alizarin, aluminon or morin (pp. 267-268).

9. Detection of Ni^{++}. Test for Ni^{++} with dimethylglyoxime in a separate portion of the ammoniacal solution, which may contain Mn^{++} and ammine complexes of nickel, cobalt, and zinc. The test is performed as in the hydrogen peroxide method (p. 306, 5b).

10. Confirmatory Tests for Zn^{++}. If zinc was not found in the preliminary tests, the solution may be slightly acidified with HCl and the tests for Zn^{++} repeated. The slightly acid solution is shaken in the cold with $CaCO_3$ powder and treated as described in 2e on p. 303.

Pyridine method

Pyridine, C_5H_5N, is a weak organic base ($K = 1.4 \times 10^{-9}$). In weakly acidic solutions it forms salts, such as $(C_5H_5NH)NO_3$,

---

* That is why they are tested for before separation into subgroups.

** If required, it may be washed, dissolved in H_2SO_4 containing 1-2 drops of KNO_2 or H_2O_2 solution (to reduce Mn^{IV}) and tested for Fe^{+++}, Mn^{++} and Co^{++} in separate portions.

*** See footnote to 10 on p. 308.

which give buffer solutions of pH $\approx$ 6.5 with excess pyridine. Table 10 (p. 128) shows that at this pH value Fe^{+++}, Al^{+++} and Cr^{+++} are completely precipitated as the hydroxides. On the other hand, Mn^{++}, Zn^{++}, Ni^{++} and Co^{++} are not precipitated at this pH but remain in solution as pyridine complexes of the type $[Me(C_5H_5N)_2]^{++}$, and may be detected in solution by the usual methods. The initial stages in the analysis are the same as in the hydrogen peroxide method (1-3, pp. 302-304) and the ammonia method (4-5, p. 310). The subsequent procedure is as follows.

6. **Separation of Al^{+++}, Cr^{+++} and Fe^{+++} from the Rest of Group III.** Take the filtrate obtained after the Group III sulphides and hydroxides had been dissolved in HNO_3 (according to 4), dilute it with water, and neutralize with Na_2CO_3 until a permanent turbidity forms. Dissolve this in 1-2 drops of 6 *N* HNO_3. Heat the slightly acid solution, add saturated NH_4NO_3, and precipitate Al^{+++}, Cr^{+++} and Fe^{+++} by addition of 20% pyridine solution. Add the pyridine drop by drop, stirring continuously with a glass rod. Confirm that the precipitation is complete and filter off the precipitate, containing $Al(OH)_3$, $Cr(OH)_3$ and $Fe(OH)_3$, without allowing the solution to cool. Note the colour of the precipitate and draw preliminary inferences concerning the possible presence of particular ions. Wash the precipitate with hot 3% NH_4NO_3 containing 1-2 drops of pyridine, and investigate it as in the ammonia method (see 7 and 8, p. 312).

The filtrate, which may contain $[Mn(C_5H_5N)_2]^{++}$, $[Zn(C_5H_5N)_2]^{++}$, $[Ni(C_5H_5N)_2]^{++}$, and $[Co(C_5H_5N)_2]^{++}$ ions, is investigated according to 7.

7. **Detection of Zn^{++}, Mn^{++}, Co^{++} and Ni^{++}.** These ions are found by the fractional method in separate portions of the filtrate from 6.

(a) **Zn^{++}.** Add an equal volume of formate buffer to a portion of the filtrate. Check the pH (it should be 2) and pass H_2S through the solution for 2-4 minutes. A white precipitate of ZnS indicates the presence of Zn^{++}. If required to confirm Zn^{++}, filter off this precipitate, dissolve it in HCl, boil out H_2S and carry out confirmatory tests (Sec. 57, 6 and 8).

(b) **Mn^{++}.** The procedure is the same as in the ammonia method (5b, p. 311).

(c) **Co^{++}.** Add saturated NH_4CNS solution and 1-2 ml of amyl alcohol to a portion of the filtrate. Shake the test tube; Co^{++} is present if the layer of amyl alcohol is blue.

(d) **Ni^{++}.** Add 3-4 ml of ammoniacal dimethylglyoxime solution to 1-2 ml of the filtrate. A bright red precipitate indicates the presence of Ni^{++}. This can also be performed as a spot test on a substrate of Na_2HPO_4 (p. 295).

Table 19

Analysis of Mixtures of Groups III-I

(ammonia method)

1. Dissolve ppt. in HCl; separate insoluble residue of $BaSO_4$, $SrSO_4$ ($CaSO_4$). Investigate as in 3, Table 12, p. 177

2. Test for NH_4^+, Fe^{+++}, Fe^{++} and Zn^{++} (in separate portions of solution)

Solution: Al^{+++}, Cr^{+++}, Fe^{+++}, Fe^{++}, Mn^{++}, Zn^{++}, Co^{++}, Ni^{++}, Group II and I cations (HCl)

3. Precipitate Group III by $(NH_4)_2S$ in presence of NH_4OH and NH_4Cl. Wash the ppt. thoroughly with water containing NH_4NO_3 to remove Cl^-

Precipitate: $Al(OH)_3$, $Cr(OH)_3$, Fe_2S_3, FeS, MnS, ZnS, CoS, NiS

4. Heat with HNO_3 to dissolve ppt. and oxidize Fe^{++}

Filtrate: Al^{+++}, Cr^{+++}, Fe^{+++}, Mn^{++}, Zn^{++}, Co^{++}, Ni^{++} (HNO_3)

5. Test for Co^{++} and Mn^{++} in separate portions of filtrate

6. Add excess NH_4OH in presence of NH_4Cl to precipitate Al^{+++}, Cr^{+++} and Fe^{+++}

Precipitate: $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$ and partially Mn and Co hydroxides

7. Treat with excess NaOH and H_2O_2 to separate Fe^{+++} from Cr^{+++} and Al^{+++}

Ppt.: $Fe(OH)_3$, $Co(OH)_3$, $MnO(OH)_2$. Not investigated

Filtrate: CrO_4^{--}, AlO_2^- (NaOH)

8. (a) Test for CrO_4^{--}
   (b) Test for Al^{+++} by adding NH_4OH to solution acidified with H_2SO_4. Confirm Al^{+++}

Filtrate: Mn^{++}, $[Zn(NH_3)_6]^{++}$, $[Ni(NH_3)_6]^{++}$, $[Co(NH_3)_6]^{++}$, excess NH_4OH and ammonium salts

9. Test for Ni^{++}

10. Precipitate Zn^{++} by H_2S in presence of formate buffer, or in presence of 0.01 *N* HCl after neutralization with $CaCO_3$

Ppt.: ZnS (possibly some CoS, NiS and S). Dissolve in HCl. Confirm Zn^{++}

Filtrate: Mn^{++}, Co^{++}, Ni^{++}, excess NH_4^+ salts. Not investigated

Filtrate: Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, K^+, Na^+, excess $(NH_4)_2S$ and other ammonium compounds. Decompose $(NH_4)_2S$ by boiling with CH_3COOH. Remove pptd. sulphur. Evaporate and ignite to remove most of the NH_4 salts. Dissolve dry residue in HCl. Test for cations of Groups II and I (Table 12)

QUESTIONS AND PROBLEMS

1. How does analytical Group III differ from (a) Groups I and II; (b) Groups IV and V?
2. Explain the difference between the effects of dilute HCl on the sulphides of Groups III and IV.
3. Why does hydrogen sulphide precipitate Cu^{++} but not Mn^{++}, whereas Na_2S solution precipitates both these cations?
4. Why is $(NH_4)_2S$ used as the Group III group reagent rather than Na_2S or K_2S?
5. Describe and explain the action of H_2S on the Zn^{++} ion. Describe how zinc may be precipitated completely from a solution containing all the cations of Groups III, II and I.
6. Why are CoS and NiS insoluble in HCl? How can they be dissolved? Give the reaction equations.
7. Explain why the sulphides of cobalt and nickel are not precipitated from acid solutions although they are insoluble in dilute HCl.
8. Explain why the oxidation state of iron must be determined before precipitation of Group III by ammonium sulphide.
9. State and explain the conditions which must be satisfied for precipitation of Group III cations.
10. Describe the reactions in which aluminium hydroxide exhibits (a) basic and (b) acidic properties.
11. By what methods can $Al(OH)_3$ be precipitated from a solution of an aluminate?
12. Describe and explain the action of $(NH_4)_2S$ and of Na_2CO_3 on salts of aluminium and of chromium (III).
13. Using the solubility products of manganese sulphide and hydroxide, calculate the ratio of OH^- and S^{--} ion concentrations in an ammonium sulphide solution which precipitates $Mn(OH)_2$ from a solution containing 1 g-ion of Mn^{++} per litre. What conclusion may be drawn from this result?

Answer. The OH^- ion concentration must be at least 1.4×10^8 as high as the S^{--} concentration.

14. Name the chromium anions formed by oxidation of Cr^{+++} in acid and in alkaline solutions. Write the equation for oxidation of $Cr_2(SO_4)_3$ by potassium permanganate in the presence of KOH.
15. Write the equation for reduction of $K_2Cr_2O_7$ by H_2S in the presence of H_2SO_4.
16. Name the substances present in the solution and the precipitate respectively when the following reagents are added to a mixture of iron (III), aluminium, chromium (III), manganese (II) and zinc salts: (a) excess NaOH in the cold; (b) excess NaOH at the boil; (c) excess NaOH and H_2O_2 at the boil; (d) excess NH_4OH; (e) sodium acetate at the boil. Illustrate your answer by equations for the reactions.
17. State and explain how $FePO_4$ and $AlPO_4$ differ from the other phosphates of Groups III and II.
18. Why can Fe^{+++} and Fe^{++} ions be detected by means of reagents containing iron?
19. Explain the solubility of (a) $Fe(OH)_2$ in NH_4Cl; (b) $Zn(OH)_2$ in NH_4OH. Why is $Al(OH)_3$ insoluble in NH_4Cl?
20. Write the equations for the following reactions: (a) oxidation of $FeCl_2$ by $KClO_3$ (which is itself reduced to KCl) in the presence of HCl; (b) reduction of $Fe_2(SO_4)_3$ by H_2SO_3.
21. What reagents may be used for oxidizing Mn^{++} to MnO_4^-? Give equations and state the conditions for the reactions.
22. With what reagents do zincates behave differently from aluminates?

23. State the methods by which Group III cations can be separated into subgroups.

24. Name the cations which must be detected separately in analysis of mixtures of Groups I, II and III, and explain why.

25. Name the compounds precipitated by the group reagent for Group III.

26. How are Co^{++} and Ni^{++} ions separated in systematic analysis? In what form is iron present in solution after this separation?

27. How is the filtrate from separation of nickel and cobalt separated further? What are the reactions of Fe^{++}, Al^{+++}, Cr^{+++}, Mn^{++} and Zn^{++} ions in this procedure?

28. Describe how the precipitate and filtrate obtained in the separation referred to in the previous question are investigated.

29. How would you analyze a mixture containing $KMnO_4$, $K_2Cr_2O_7$ and $AlCl_3$?

30. Suppose that a solution may contain all the cations of Groups III, II and I, but we are concerned only with the presence of Mn^{++}, Cr^{+++} and Co^{++}. Describe how these ions may be detected by fractional tests.

CHAPTER V

CATIONS OF GROUP IV

THEORETICAL ASPECTS

In this chapter the reactions and analytical procedures for Group IV cations are studied, and the presentation of the theory of oxidation-reduction processes is completed. At this stage we examine oxidation potentials, which are very important in chemistry, and discuss the direction of oxidation-reduction reactions, the influence of the reaction of the medium and of concentrations on these reactions, and the equilibrium constants of oxidation-reduction processes.

61. Oxidation Potentials

When studying various oxidation-reduction processes we continuously find that while one oxidizing agent readily oxidizes a given substance or ion, another cannot effect this reaction. For example, while free Cl_2 oxidizes Br^- ions according to the equation

$$Cl_2 + 2Br^- = Br_2 + 2Cl^-$$

the Fe^{+++} ion cannot oxidize Br^- ions to Br_2. However, we saw (p. 276, 7) that it easily oxidizes I^- ions:

$$2I^- + 2Fe^{+++} = I_2 + 2Fe^{++}$$

These facts evidently show that different oxidizing and reducing agents differ in "strength", i.e., in chemical activity. For example, Cl_2 is a stronger oxidizing agent than the Fe^{+++} ion. The I^- ion, which can reduce Fe^{+++} to Fe^{++}, is a stronger reducing agent than Br^-, which cannot reduce the Fe^{+++} ion, etc.

An oxidizing agent gains electrons in an oxidation-reduction reaction while a reducing agent gives up electrons. Therefore these differences in the strengths of various oxidizing or reducing agents are associated with unequal tendencies of certain atoms or ions in them to gain or lose electrons. *The greater the tendency of an atom or ion to lose electrons, the stronger an oxidizing agent it is; the greater the tendency of an atom or ion to gain electrons, the higher is its activity as a reducing agent.*

A quantitative measure of the tendency of various atoms or ions to lose or gain electrons is given by studies of the reactions in

voltaic (galvanic) cells (Sec. 50). The experimentally determined electromotive force (emf) of a cell, which is the potential difference between its two constituent half-cells, is a measure of the tendency of electrons to pass from atoms (or ions) of the reducing agent to atoms (or ions) of the oxidizing agent, just as the difference between the gaseous pressures in two interconnected vessels is a measure of the tendency of the gas to flow from one vessel into the other.

A most important feature of the design of such cells is that the oxidizing and the reducing agents are contained separately in different vessels, so that electrons can be transferred only along a conductor connecting the two vessels.

Moreover, as in the internal circuit electricity can be carried only by ions, these ions must be able to diffuse from one vessel into the other. Such diffusion is possible if either (a) the vessels are separated by a porous partition or (b) they are connected by a so-called electrolytic bridge. This is an inverted U-tube containing a solution of an electrolyte (usually KCl).

For example, a cell which yields current a sthe result of the reaction

$$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$$

or

$$Sn^{++} + 2Fe^{+++} = Sn^{++++} + 2Fe^{++} \qquad (1)$$

can be constructed by the method described on p. 241 (see Fig. 28).

During the operation of this cell the reaction (1) may be regarded as *chemical action at a distance*, as the oxidizing agent (Fe^{+++} ions) and the reducing agent (Sn^{++} ions) do not come into direct contact. Of course, the same reaction can be effected by simple mixing of $FeCl_3$ and $SnCl_2$ solutions, but in this case the chemical energy liberated by the reaction is converted into heat and not into electrical energy.

The action of this cell may be schematically represented as follows:

$$+(Pt) \longrightarrow 2Fe^{+++}/2Fe^{++} \,||\, Sn^{++++}/Sn^{++} \longrightarrow (Pt)-$$

Reduction (→) Oxidation (←)

The scheme shows that electron loss or oxidation occurs at the negative pole of the cell, while at the positive pole electrons are gained, i.e., reduction occurs.

Since electron transfer occurs in every oxidation-reduction process, various other oxidation-reduction reactions may be used for constructing cells. Any cell obtained in this way has (for given concentrations of the reacting substances) a definite electromotive force (emf), which is the potential difference between its constituent half-cells. *This emf is a measure of the tendency of electrons to pass*

from the atoms (or ions) of the reducing agent to the atoms (or ions) of the oxidizing agent. Therefore studies of the emf of various cells give an indication of the relative strengths of various oxidizing or reducing agents.

The individual half-cells comprising a cell always contain not only the particular oxidizing (or reducing) agent but also the substances formed in the reaction. For example, in the cell shown in Fig. 28 the vessel *2* contains not only the original Sn^{++} ions but also the Sn^{++++} ions formed from them by the reaction. These two ions, which represent different degrees of oxidation of the same chemical element (tin), comprise an *oxidation-reduction couple* (or system), written as Sn^{++++}/Sn^{++}; it forms one of the half-cells of the given cell. The second half-cell is the oxidation-reduction couple Fe^{+++}/Fe^{++}.

Every oxidation-reduction couple contains an *oxidized form*, consisting of the element in a higher valency state (Sn^{++++}, Fe^{+++}), and the reduced form, in a lower valency state (Sn^{++}, Fe^{++}). The oxidized form in every such couple is the oxidizing agent, and the reduced form is the reducing agent.

In order to obtain a quantitative measure of the strengths of various oxidizing and reducing agents from the emf of a cell composed of two oxidation-reduction couples, we must always use the same standard couple in conjunction with the individual couples. The standard system used for this purpose is the couple $2H^+/H_2$ in which the H^+ ion concentration (or, more precisely, the activity) is 1 g-ion/litre and the gaseous hydrogen pressure is 1 atm. This is known as the *standard hydrogen electrode.*

An apparatus for determining standard oxidation potentials is shown in Fig. 35. The vessel *1* contains H_2SO_4 solution of the required concentration, and a platinum electrode covered electrolytically with a layer of finely divided platinum ("platinum black") is immersed in it. Chemically pure hydrogen is passed into the solution through the tube *4*; when the hydrogen comes into contact with the platinum electrode, it is adsorbed by the finely divided platinum. Accordingly, the electrode behaves as if it was made of hydrogen.

The potential of the standard hydrogen electrode is taken arbitrarily as zero, just as the temperature of melting ice is taken as zero for temperature measurements.

Therefore if we combine, as shown in Fig. 35, a standard hydrogen electrode with some other couple, such as Fe^{+++}/Fe^{++}, and measure the emf of the resultant cell with the special instrument *5* (called a potentiometer), this emf represents the potential of the given couple on our arbitrary scale. It has been found experimentally that when $[Fe^{+++}] = [Fe^{++}]$, the potential (E) is

$$E_{Fe^{+++}/Fe^{++}} = +0.77 \text{ V}$$

The sign of the potential indicates that the given couple acts as the positive pole in the cell, while the standard hydrogen electrode is the negative pole. Since the negative pole yields electrons,

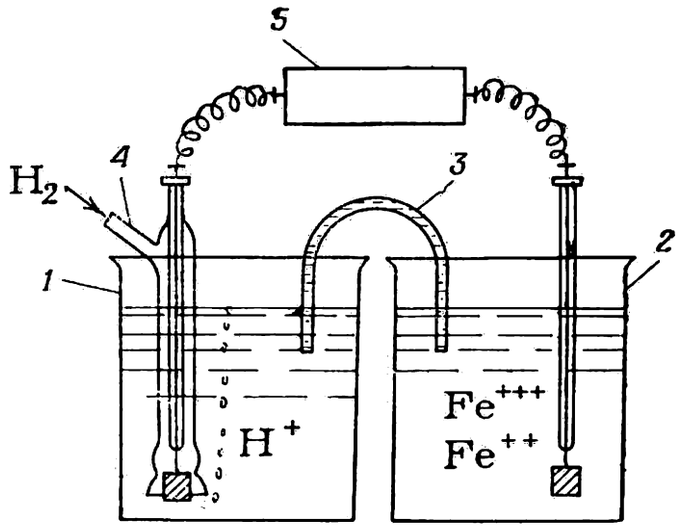


Fig. 35. Determination of the standard oxidation potential of the Fe^{+++}/Fe^{++} system
1, *2*—beakers; *3*—electrolytic bridge; *4*—gas-delivery tube; *5*—potentiometer

emitting them into the circuit, while the positive pole gains them, the following chemical processes must occur in the cell:

in the vessel *1*

$$H_2 - 2e = 2H^+$$

in the vessel *2*

$$2Fe^{+++} + 2e = 2Fe^{++}$$

The overall equation for the reaction is

$$2Fe^{+++} + H_2 = 2H^+ + 2Fe^{++}$$

If, instead of Fe^{+++}/Fe^{++}, we combine the couple $Cl_2/2Cl^-$ with the standard hydrogen electrode, we find that its potential* is

$$E_{Cl_2/2Cl^-} = +1.36 \text{ V}$$

This means that the following reaction takes place in the cell:

$$H_2 + Cl_2 \overset{2e}{=} 2H^+ + 2Cl^-$$

* This half-cell is made up in the same way as the standard hydrogen electrode, except that instead of H_2SO_4 we use HCl solution in which the Cl^- ion concentration (more accurately, activity) is 1 g-ion/litre, and Cl_2 is passed instead of H_2. To avoid chemical action of chlorine on the platinum electrode, the gaseous chlorine pressure must be considerably less than 1 atm. The emf found in this way is converted to a pressure of 1 atm by means of a special formula.

As in the preceding case, the reaction consists essentially of removal of electrons from free H_2, but the oxidizing agent removing these electrons is gaseous Cl_2 instead of Fe^{+++} ions. The emf of the cell in the latter case (+1.36 V) is considerably greater than in the former (+0.77 V); we must therefore conclude that Cl_2 has a higher tendency to gain electrons and is therefore a much stronger oxidizing agent than Fe^{+++}. However, these values give us more than merely the strengths of the oxidizing agents in the respective couples. They also give an indication of the relative strengths of the corresponding reducing agents, Fe^{++} and Cl^- ions.

Indeed, when we say, for example, that Cl_2 is a powerful oxidizing agent we mean that its atoms have a strong tendency to gain electrons, i.e., to be converted into Cl^- ions. This means that Cl^- ions must hold these electrons firmly, so that they are a very weak reducing agent. Conversely, the potential of the Fe^{+++}/Fe^{++} couple is less than that of $Cl_2/2Cl^-$. Therefore Fe^{++} ions, formed when Fe^{+++} ions gain electrons, hold these electrons less firmly and are therefore a stronger reducing agent than Cl^-.

Thus, we see that the potentials of oxidation-reduction couples measured agaist a standard hydrogen electrode give an indication of the oxidizing and reducing activity of their constituent oxidizing and reducing agents.

The higher the potential of a given couple, the stronger an oxidizing agent is the corresponding oxidized form, and the weaker a reducing agent is the reduced form.

Since the strength of oxidizing agents increases with increasing potential, these potentials are known as *oxidation potentials**.

It is evident that the oxidized form of the $2H^+/H_2$ couple, i.e., H^+ ions, is an even weaker oxidizing agent than Fe^{+++} ions, while free H_2 is a more powerful reducing agent than Fe^{++} ions. Since the oxidation potential** of the Zn^{++}/Zn couple is

$$E_{Zn^{++}/Zn} = -0.76 \text{ V}$$

it follows that Zn^{++} ions are even a weaker oxidizing agent than H^+ ions and metallic zinc is an even stronger reducing agent than hydrogen gas.

---

* However, this terminology is not consistently used. These potentials are often also called "oxidation-reduction" or "redox" potentials. The word "redox" is formed from the initial syllables of the words *reduction* and *oxidation*.

** The negative sign of this potential means that in combination with a standard hydrogen electrode this couple acts as the negative pole of the cell while $2H^+/H_2$ is the positive pole. Therefore the following reaction occurs in the cell:

$$Zn + 2H^+ \xrightarrow{2e} H_2 + Zn^{++}$$

It should be remembered that the potentials of such couples depend not only on the nature of their constituent oxidizing and reducing agents but also on their concentrations. The effects of the concentrations of the oxidizing and reducing agents on the oxidation potential are not difficult to predict. For example, it is evident that the oxidizing activity of Fe^{+++} ions must increase with increasing concentration of these ions in solution and with decreasing concentration of Fe^{++} ions, which are the product of the reaction and which therefore favour the reverse process. It follows that the oxidation potential of this couple must increase with increase of the $\frac{[Fe^{+++}]}{[Fe^{++}]}$ ratio, or, in general, with increase of the ratio of the concentrations of the oxidized and reduced forms.

The quantitative relationship between the oxidation potential and this ratio can be represented by the Nernst equation, based on the laws of thermodynamics:

$$E = E_0 + \frac{RT}{nF} \ln \frac{[ox]}{[red]} \qquad (2)$$

where E = oxidation potential (volts)
[ox] = concentration (more correctly, the activity) of the oxidized form
[red] = concentration (activity) of the reduced form
R = gas constant (8.313 joules)
T = absolute temperature
F = the Faraday number (96,500 coulombs)
n = number of electrons gained (or lost) when the oxidized form is converted into the reduced form (or *vice versa*)
E_0 = *standard oxidation potential* of the couple, i.e., its potential when [ox] = [red]*.

When [ox] = [red], $\ln \frac{[ox]}{[red]}$ is zero, and in Eq. (2) $E = E_0$.

Putting in the numerical values of the constants and converting to common logarithms, we have for 18°:

$$E = E_0 + \frac{0.058}{n} \log \frac{[ox]}{[red]} \qquad (3)$$

For the couple Fe^{+++}/Fe^{++} the potential can be calculated from the formula

$$E_{Fe^{+++}/Fe^{++}} = 0.77 + \frac{0.058}{1} \log \frac{[Fe^{+++}]}{[Fe^{++}]}$$

---

* In all the above numerical examples the standard oxidation potentials are meant.

For example, if $[Fe^{+++}]$ is 1 g-ion/litre and $[Fe^{++}]$ is 0.0001 g-ion/litre, we have

$$E_{Fe^{+++}/Fe^{++}} = 0.77 + \frac{0.058}{1} \log 10^4 = 1.002 \text{ V}$$

If the equation for the reaction taking place when the oxidized form is converted into the reduced form contains coefficients which are not equal to unity, the concentrations of the respective components must be raised to the corresponding powers. For example, for $Br_2/2Br^-$

$$E = E_0 + \frac{0.058}{2} \log \frac{[Br_2]}{[Br^-]^2}$$

In cases such as Zn^{++}/Zn, when the reduced form is a metal (a solid phase) its concentration is constant and is therefore omitted from the expression for E. Then

$$E_{Zn^{++}/Zn} = E_0 + \frac{0.058}{2} \log [Zn^{++}]$$

Evidently E_0 is the potential (—0.76 V) of the couple when $[Zn^{++}] = 1$ g-ion/litre, as only then $\log [Zn^{++}] = 0$ and $E = E_0$.

So far we have examined applications of the Nernst equation to oxidation-reduction reactions in which simple (elementary) ions act as the oxidizing or reducing agents. These ions alter only in charge in the reactions, while their composition remains unchanged. Sometimes ions consisting of several atoms are involved in oxidation-reduction reactions. For example, the $[Fe(CN)_6]^{---}$ ion is reduced to $[Fe(CN)_6]^{==}$ when it oxidizes some other ion or element; MnO_4^{--} ions are oxidized to MnO_4^-. However, more usually such ions undergo extensive changes in composition as the result of oxidation or reduction. For example, in oxidation reactions in acid solution MnO_4^- anions are converted into Mn^{++} cations, $Cr_2O_7^{--}$ anions into Cr^{+++} cations, AsO_4^{---} anions into AsO_2^- anions, etc. These changes are represented by the equations*

$$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{++} + 4H_2O$$

$$Cr_2O_7^{--} + 14H^+ + 6e \rightleftarrows 2Cr^{+++} + 7H_2O$$

$$AsO_4^{---} + 4H^+ + 2e \rightleftarrows AsO_2^- + 2H_2O, \text{ etc.}$$

These examples show that an enormous part in such changes of multiatomic ions in the course of reduction or oxidation is played by hydrogen ions, which combine with oxygen atoms of these ions to give water molecules. It is obvious that in such cases the course of the oxidation-reduction process and the magnitude of the oxidation

* The method for deriving such equations is discussed in Sec. 50.

potential of the corresponding couple must depend on the H^+ ion concentration in solution. This concentration is included in the numerator of the fraction after the logarithm sign in the equation, raised to a power equal to the coefficient of H^+ in the reaction equation. In the present instance

$$E_{MnO_4^-/Mn^{++}} = E_0 + \frac{0.058}{5} \log \frac{[MnO_4^-] \cdot [H^+]^8}{[Mn^{++}]}$$

Thus, variations of the H^+ ion concentration have a particularly strong influence on the oxidation potential of the given couple, and hence on the oxidizing activity of the MnO_4^- ion; this activity increases rapidly with rise of the H^+ ion concentration.

It follows from the above equation that this couple has the standard potential value when $[MnO_4^-] = [Mn^{++}]$ and $[H^+] = 1$ g-ion/litre, as only under these conditions $E = E_0$.

62. Direction of Oxidation-Reduction Reactions

The standard oxidation potentials E_0 in the Nernst equation have been determined for a large number of systems. The most important are given in Table 20 (a fuller table is given in Appendix, Table VIII).

The first and third columns of Table 20 (and of Table VIII) give the formulas of the individual components of the various couples; these components are in the order of increasing standard oxidation potentials E_0 (fourth column). The second column gives the number of electrons (n) lost or gained when the reducing agent (first column) is converted into the corresponding oxidizing agent (third column), or *vice versa*.

Since the strength of oxidizing agents increases and that of reducing agents decreases with increasing oxidation potential, the strongest oxidizing agents are at the bottom of the third column, and the strongest reducing agents, at the top of the first column.

For example, the strongest oxidizing agent of all is free F_2 (see Appendix, Table VIII), corresponding to the highest E_0 (+2.85 V). Other very powerful oxidizing agents include ozone O_3 (+1.90 V), sodium bismuthate $NaBiO_3$ (>+1.80 V), ammonium persulphate $(NH_4)_2S_2O_8$ (> +1.80 V), hydrogen peroxide (+1.80 V), potassium permanganate $KMnO_4$ in acid solution (+1.51 V), free Cl_2 (+1.36 V), ions of the noble metals Au^+, Au^{+++}, Ag^+, etc.

The strongest reducing agents include the alkali and alkaline earth metals, and metals such as Mg, Al, Zn, etc. Among the ions, the S^{--} anion is a very powerful reducing agent ($E_0 = -0.51$ V); Sn^{++}, SO_3^{--}, I^-, Fe^{++}, etc., are weaker in this respect. Fluoride ions, F^-, have no reducing properties, as no oxidizing agent can remove

Table 20

Standard Oxidation Potentials

Symbols: (g)—gas; (liq)—liquid; (s)—solid

Reduced form (reducing agents)	Number of electrons	Oxidized form (oxidizing agents)	Potential E_0, V
Zn (s)	2*e*	Zn^{++}	—0.76
S^{--}	2*e*	S (s)	—0.51
Fe (s)	2*e*	Fe^{++}	—0.44
Sn (s)	2*e*	Sn^{++}	—0.14
Pb (s)	2*e*	Pb^{++}	—0.13
Fe (s)	3*e*	Fe^{+++}	—0.04
H_2 (g)	2*e*	$2H^+$	—0.00
Sn^{++}	2*e*	Sn^{++++}	+0.15
$SO_3^{--} + H_2O$	2*e*	$SO_4^{--} + 2H^+$	+0.22
Cu (s)	2*e*	Cu^{++}	+0.34
$2I^-$	2*e*	I_2 (s)	+0.54
Fe^{++}	1*e*	Fe^{+++}	+0.77
NO (g) $+ 2H_2O$	3*e*	$NO_3^- + 4H^+$	+0.95
NO (g) $+ 2H_2O$	1*e*	$HNO_2 + H^+$	+0.98
$2Br^-$	2*e*	Br_2 (liq)	+1.07
$2Cl^-$	2*e*	Cl_2 (g)	+1.36
$Mn^{++} + 4H_2O$	5*e*	$MnO_4^- + 8H^+$	+1.51
$2F^-$	2*e*	F_2	+2.85

electrons from them. We know that electrons can be removed from F^- ions only by electrolysis.

Knowing the relative strengths of various oxidizing and reducing agents, we can determine the directions of reactions between them. For example, suppose that we want to predict the direction of the reaction

$$2Fe^{+++} + Sn^{++} = Sn^{++++} + 2Fe^{++}$$

i. e., to find whether it results in oxidation of Sn^{++} ions by Fe^{+++} to give Sn^{++++}, or the reverse.

The oxidation potential of Fe^{+++}/Fe^{++} (+0.77 V) is higher than that of Sn^{++++}/Sn^{++} (+0.15 V). Therefore if these couples are combined in a cell, the Sn^{++++}/Sn^{++} couple would be the negative pole, and Fe^{+++}/Fe^{++} the positive pole. This means that the following processes would occur in the cell:

$$Sn^{++} - 2e = Sn^{++++}$$
$$2Fe^{+++} + 2e = 2Fe^{++}$$

i.e., the reaction

$$Sn^{++} + 2Fe^{+++} \longrightarrow Sn^{++++} + 2Fe^{++}$$

If the corresponding substances are simply mixed, the reaction would proceed in the same direction outside the cell.

It is easy to see that *in any oxidation-reduction process a new oxidizing and a new reducing agent are formed from the original reducing and oxidizing agents*:

$$Ox_1 + Red_2 = Red_1 + Ox_2$$

and the new agents are weaker than the original ones. For example, in the case discussed above, in accordance with the standard oxidation-reduction potentials of Sn^{++++}/Sn^{++} and Fe^{+++}/Fe^{++}, the oxidizing agent (Sn^{++++}) and the reducing agent (Fe^{++}) formed are weaker than the original agents (Fe^{+++} and Sn^{++}). The same applies to all other oxidation-reduction reactions. Accordingly, we can formulate the following rule: *oxidation-reduction reactions always lead to the formation of weaker oxidizing and reducing agents from stronger ones*; *never the reverse.*

This rule can be used for deciding the direction of such reactions. In other words, any oxidizing agent can oxidize all the reducing agents with lower oxidation potentials above it in the table. Conversely, any reducing agent can reduce all the oxidizing agents with higher oxidation potentials below it in the table.

Note the undoubted analogy between oxidation-reduction processes and protolytic reactions (see Sec. 31). We see that:

(a) oxidation-reduction reactions are accompanied by transfer of electrons, and protolytic reaction by transfer of protons;

(b) in any oxidation-reduction reaction a new reducing and a new oxidizing agent are formed from the original oxidizing and reducing agents; similarly, in a protolytic reaction a new base and a new acid are formed from the original acid and base:

$$Ox_1 + Red_2 = Ox_2 + Red_1$$

$$Acid_1 + Base_2 = Acid_2 + Base_1$$

(c) the strength of a reducing agent increases with increasing tendency to lose electrons, and that of an oxidizing agent increases with increasing tendency to gain electrons. Similarly, according to the protolytic theory, the strength of an acid increases with increasing tendency to lose protons, and that of a base with its tendency to gain protons;

(d) a strong oxidizing agent on gaining electrons is converted into a weak reducing agent and *vice versa*. In the same way, a strong base on gaining protons becomes a weak acid, and a weak acid on losing protons becomes a strong base.

Let us consider some examples of the application of this rule.

1. Table 20 shows that metallic Zn ($E_0 = -0.76$ V) is a stronger reducing agent than Pb ($E_0 = -0.13$ V) or Cu ($E_0 = +0.34$ V). Therefore the following reactions should take place if we act with

metallic zinc on solutions of lead or copper salts:

$$Pb^{++} + Zn = \downarrow Pb + Zn^{++}$$

$$Cu^{++} + Zn = \downarrow Cu + Zn^{++}$$

because these reactions yield weaker reducing agents (Pb or Cu) by the action of a stronger one (Zn). Conversely, Pb or Cu cannot reduce Zn^{++} ions to free Zn, as this would contradict the above rule.

If we arrange all the metals in order of increasing standard oxidation potentials of the corresponding couples, we obtain the *potential series of the metals*, familiar from the course of inorganic chemistry:

Li, K, Ba, Ca, Na, Sr, Mg, Al, Mn, Zn, Fe, Cd, Co, Ni, Sn, Pb, H, Cu, Sb, Bi, Hg, Ag, Pt, Au

The metals furthest to the left in this series are the strongest reducing agents and have the highest chemical activity. As a rule, no metal can displace (i.e., reduce) any other metal to its left in the series from solutions of its salts. Conversely, many of the metals can displace metals on their right. In particular, all metals to the left of hydrogen can liberate hydrogen from acid solutions and are therefore soluble in acids. On the other hand, metals to the right of hydrogen are insoluble in dilute acids (apart from nitric acid, which dissolves most metals owing to the oxidizing action of NO_3^- ions).

2. As a further example, let us consider the action of various oxidizing agents on I^-, Br^-, and Cl^- ions. It was stated earlier that Br^- ions can be oxidized to Br_2 by free Cl_2 but not by Fe^{+++} ions. This is easily understood if we note the positions of Cl_2, Br_2 and Fe^{+++} in the table of oxidation potentials. We see that Br_2 is a weaker oxidizing agent than Cl_2 but stronger than Fe^{+++}. Therefore the reaction

$$Cl_2 + 2Br^- = 2Cl^- + Br_2$$

obeys the above rule. On the other hand, the reaction

$$2Fe^{+++} + 2Br^- = Br_2 + 2Fe^{++}$$

would not obey the rule, because it would yield a stronger oxidizing agent (Br_2) and a stronger reducing agent (Fe^{++}) from weaker ones (Fe^{+++} and Br^-). Conversely, the reverse reaction

$$2Fe^{++} + Br_2 = 2Fe^{+++} + 2Br^-$$

should proceed readily; this is found to be the case.

Similarly, we find from the table of standard oxidation potentials that nitrous acid (which has a higher standard oxidation potential than I_2 and lower than Br_2) can oxidize I^- but not Br^- ions.

In contrast to nitrous acid, permanganate ions in acid solution ($E_0 = +1.51$ V) should evidently oxidize not only I^- but also Br^- and Cl^- ions. It is clear that free Br_2 can oxidize I^- but not Cl^- ions, while free Cl_2 oxidizes both I^- and Br^- ions.

3. It often happens in analysis that the unknown solution contains more than one reducing agent (for example, Br^- and I^- ions) capable of reacting with an added oxidizing agent (for example, Cl_2 solution). This raises the question of the sequence in which these reducing agents are oxidized.

Turning to the table, we readily see that Br^- ions can start to be oxidized only after the I^- ions have been oxidized. Indeed, if Br^- ions were oxidized first, free Br_2 would appear in solution. According to its position in the table, free bromine should immediately oxidize I^- ions and be itself reduced back to Br^- ions. In the same way we find that in a solution containing Br^- and I^- ions together with stronger reducing agents (such as S^{--}, SO_3^{--}, or $S_2O_3^{--}$ ions, etc.) oxidation of I^- ions cannot begin until these stronger reducing agents have been oxidized almost completely. This must be taken into account in detection of I^- and Br^- ions.

From all this we may conclude that *any oxidizing agent first attacks the strongest reducing agent present. Any reducing agent first attacks the strongest oxidizing agent.*

In other words, of all the oxidation-reduction processes possible under given conditions, the first to occur is usually the one corresponding to the largest difference of oxidation potentials.

Therefore, for example, if we add metallic Fe to $SnCl_4$ solution the following reaction occurs:

$$SnCl_4 + Fe = SnCl_2 + FeCl_2$$

but Sn^{++++} would not be reduced to metallic tin, as the latter reaction corresponds to a smaller potential difference (0.43 V) than reduction to Sn^{++} ions (0.59 V).

4. Finally, suppose that we dissolve metallic iron in dilute HNO_3 and want to find the equation for the reaction. How can this question be answered with the aid of Table 20?

First we note that two oxidizing agents are present: H^+ ions and NO_3^- ions. The latter are considerably below H^+ in the table and have much higher oxidizing activity. Therefore, in accordance with the above rule, we should put NO_3^- and not H^+ ions in the required equation.

Further, we must decide whether $Fe(NO_3)_2$ or $Fe(NO_3)_3$ is formed in the reaction. It is not difficult to see that although the formation of the former of these substances should correspond to a greater potential difference (1.39 V) than the formation of $Fe(NO_3)_3$ (0.99 V), nevertheless in the presence of excess HNO_3 the compound

formed must be $Fe(NO_3)_3$. The Fe^{++} ions initially formed are subsequently oxidized to Fe^{+++} by excess nitric acid. Therefore the required equation is

$$Fe + 4HNO_3 = Fe(NO_3)_3 + NO\uparrow + 2H_2O$$

63. Influence of Concentration and of the Reaction of the Medium

The examples discussed in the preceding section show that with the aid of the table of oxidation potentials we can determine the directions of oxidation-reduction processes, choose the most suitable oxidizing or reducing agents, and solve a number of other problems very important in chemistry.

It must not be forgotten, however, that the potentials given in this table are the standard values, which relate to definite concentrations, and the values should alter with change of concentration. As a result, the direction of a reaction may be completely reversed.

Consider the following example. The values of E_0 for Sn^{++}/Sn (—0.14 V) and Pb^{++}/Pb (—0.13 V) suggest that metallic tin should reduce Pb^{++} ions:

$$Pb^{++} + Sn \longrightarrow Pb + Sn^{++}$$

If the Pb^{++} ion concentration is decreased to 0.1 g-ion/litre, it can easily be calculated from the Nernst equation that the oxidation potential of Pb^{++}/Pb falls to about —0.16 V, which is below the value for Sn^{++}/Sn (—0.14 V). Therefore at the stated concentrations of Sn^{++} (1 g-ion/litre) and Pb^{++} (0.1 g-ion/litre) the reaction is reversed:

$$Pb + Sn^{++} \longrightarrow Sn + Pb^{++}$$

Evidently the direction of this reaction is reversed by such a relatively small change in the concentration of one of the ions because the difference between the standard oxidation potentials of the two couples is small (0.01 V). For the reaction

$$2Ag^+ + H_2 = 2H^+ + 2Ag$$

the difference is 0.80 V, and this reaction is reversed only as the result of a very large decrease in the concentration of Ag^+ ions. However, such a decrease can be achieved if the reaction yields a very insoluble salt or a silver complex of a low degree of dissociation. Suppose, for example, that we act with 1 *M* hydriodic acid solution on metallic silver. Since the solubility product of AgI is about 1×10^{-16} and the I^- ion concentration in the solution is 1 g-ion/litre, the Ag^+ ion concentration cannot exceed 1×10^{-16} g-ion/litre.

At this Ag^+ concentration the oxidation potential of the Ag^+/Ag couple is

$$E_{Ag^+/Ag} = 0.80 + 0.058 \log 10^{-16} = -0.13 \text{ V}$$

The negative value of this oxidation potential shows that under the stated conditions the above reaction must proceed from right to left. Therefore silver can displace hydrogen from solutions of hydriodic acid (and also of hydrogen sulphide) although it is to the right of hydrogen in the potential series and therefore cannot displace it from solutions of other acids. Many similar examples could be cited to illustrate the influence of precipitation (or complex formation) on the direction of oxidation-reduction processes.

It was pointed out above that if H^+ ions are involved in an oxidation-reduction reaction, their concentration also has a very strong influence on the oxidation potential. Therefore a change of hydrogen ion concentration can also result in reversal of the reaction. For example, according to the values of the oxidation potentials of AsO_3^{---}/AsO_4^{---} (+0.57 V) and $I_2/2I^-$ (+0.54 V), AsO_4^{---} ions should oxidize I^- to I_2:

$$AsO_4^{---} + 2I^- + 2H^+ = AsO_3^{---} + I_2 + H_2O$$

This reaction does occur if the AsO_3^{---} and AsO_4^{---} ion concentrations are equal and if $[H^+] = 1$ (or higher).

Suppose, however, that the reaction is carried out in the presence of excess $NaHCO_3$, solutions of which have pH ≈ 8. The consequent fall of the H^+ ion concentration to 1×10^{-8} g-ion/litre has no effect on the oxidation potential of $I_2/2I^-$. On the other hand, in the case of the couple AsO_4^{---}/AsO_3^{---}, where H^+ ions are involved in the conversion of the oxidized to the reduced form, as follows from the equation

$$AsO_4^{---} + 2H^+ + 2e \rightleftarrows AsO_3^{---} + H_2O$$

the oxidation potential falls to*

$$E_{AsO_4^{---}/AsO_3^{---}} = 0.57 + \frac{0.058}{2} \log \frac{[AsO_4^{---}] \cdot [H^+]^2}{[AsO_3^{---}]} =$$

$$= 0.57 + \frac{0.058}{2} \log [10^{-8}]^2 = 0.11 \text{ V}$$

Since $0.11 < 0.54$, the reaction is reversed under these conditions, and is represented by the equation

$$AsO_3^{---} + I_2 + H_2O = AsO_4^{---} + 2H^+ + 2I^-$$

This example shows that *if* H^+ *ions are consumed in a reaction, it must be conducted in acid solution. Conversely, if they are formed*

* The AsO_4^{---} and AsO_3^{---} concentrations are assumed equal.

in the reaction they must be removed by addition of alkali or substances such as $NaHCO_3$. Since the H^+ and OH^- ion concentrations are connected by the relationship

$$[H^+]\cdot[OH^-]=K_{H_2O}$$

the expenditure of OH^- ions in a reaction is equivalent to formation of H^+ ions, and formation of OH^- is equivalent to consumption of H^+.

If neither H^+ nor OH^- ions are involved in a given reaction, changes in their concentrations do not influence the course of the reaction (provided that no side reactions occur, such as precipitation of cations involved in the reaction in the form of hydroxides).

All these conclusions can also be derived from the law of mass action.

As was pointed out on p. 323, H^+ ions are usually removed in the course of oxidation reactions effected by anions of oxyacids, the oxygen atoms of which combine with hydrogen ions to give water molecules. Therefore acidity of the solution plays a very important part in these reactions. This is illustrated by the following experiments.

1. Mix solutions of KI and KNO_2 in a test tube. Although the standard oxidation potential of the NO_2^- ion (0.98 V) is greater than that of I_2 (0.54 V), I^- ions are not oxidized to I_2. However, as soon as a small amount of H_2SO_4 or HCl is added to the solution a violent reaction begins, accompanied by evolution of NO and formation of a dark brown precipitate of iodine:

$$2I^- + 2NO_2^- + 4H^+ = \downarrow I_2 + 2NO \uparrow + 2H_2O$$

Similarly, in alkaline or neutral solutions (i.e., at H^+ ion concentration of 1×10^{-7}) I^- ions do not react with most other oxidizing anions containing oxygen, such as CrO_4^{--}, IO_3^-, BrO_3^-, ClO_3^-, AsO_4^{---}, etc. When the solutions are acidified, I^- ions are oxidized to I_2.

2. Mix solutions of K_2CrO_4 and Na_2S. No change takes place. If the mixture is acidified, the following reaction occurs:

$$3S^{--} + 2CrO_4^{--} + 16H^+ = \downarrow 3S + 2Cr^{+++} + 8H_2O$$

In the same way, other reducing anions such as Cl^-, Br^-, I^-, SO_3^{--}, $S_2O_3^{--}$, CNS^-, $C_2O_4^{--}$, AsO_3^{---}, etc., are oxidized by CrO_4^{--} anions in acid solution only.

In contrast to CrO_4^{--} and NO_2^- ions and a number of other oxidizing agents, the MnO_4^- ion can act as an oxidizing agent in alkaline (or neutral) as well as in acid solution. However, the reduction products are different in the two cases. We know that in an oxidation-reduction reaction in acid solution the MnO_4^- ion gains five

electrons and is reduced to the Mn^{++} cation. In alkaline (or neutral) solution it gains only three electrons and is reduced to MnO_2, or, more correctly to its hydrated form $MnO(OH)_2$, which appears as a brown precipitate. Accordingly, there is a very large difference between the oxidizing activities of permanganate in acid and alkaline solutions, as is clear from a comparison of the standard oxidation potentials of MnO_4^-/Mn^{++} ($E_0 = 1.51$ V) and MnO_4^-/MnO_2 ($E_0 = 0.54$ V).

The difference in the reduction of MnO_4^- in acid and alkaline solutions becomes clear if we consider the equation for the reduction of MnO_2 to Mn^{++}:

$$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{++} + 2H_2O$$

This equation shows that in acid solution Mn^{++} ions, the lowest state of oxidation of manganese, constitute the more stable form. If MnO_2 was first formed in the reaction, under the influence of the higher H^+ ion concentration it would be reduced further, to Mn^{++} cations. Conversely, in alkaline or neutral solution the equilibrium is shifted towards the formation of $MnO(OH)_2$. It is therefore not surprising that this last compound is the final reduction product of the MnO_4^- ion under these conditions.

64. Equilibrium Constants of Oxidation-Reduction Reactions

The fact that oxidation-reduction reactions may proceed in either direction is evidently the consequence of the reversibility of such reactions. We know that reversible reactions lead to chemical equilibrium. The constant for this equilibrium is easy to calculate if we know the standard oxidation potentials of both oxidation-reduction couples.

Consider the reaction

$$Sn^{++} + 2Fe^{+++} \rightleftarrows Sn^{++++} + 2Fe^{++}$$

First, we write the expressions for the oxidation potentials of Sn^{++++}/Sn^{++} and Fe^{+++}/Fe^{++}:

$$E_{Sn^{++++}/Sn^{++}} = 0.15 + \frac{0.058}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]} \quad (1)$$

$$E_{Fe^{+++}/Fe^{++}} = 0.77 + 0.058 \log \frac{[Fe^{+++}]}{[Fe^{++}]} \quad (2)$$

These equations show that, as the Sn^{++++} and Fe^{++} ion concentrations increase and the Fe^{+++} and Sn^{++} concentrations decrease as the result of the reaction, the potential of the first couple, the smaller at first, gradually increases while the potential of the second decreases. Eventually the two potentials become equal.

However, we know that electron transfer is possible only if a difference of potentials exists, and must cease when the difference disappears. Therefore, when

$$E_{Sn^{++++}/Sn^{++}} = E_{Fe^{+++}/Fe^{++}}$$

equilibrium becomes established. Putting into this equation the values for $E_{Sn^{++++}/Sn^{++}}$ and $E_{Fe^{+++}/Fe^{++}}$ from Eqs. (1) and (2), we have:

$$0.15 + \frac{0.058}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]} = 0.77 + 0.058 \log \frac{[Fe^{+++}]}{[Fe^{++}]}$$

and hence

$$\frac{0.058}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]} - 0.058 \log \frac{[Fe^{+++}]}{[Fe^{++}]} = 0.77 - 0.15 \qquad (3)$$

We transform the second term in the left-hand side of this equation as follows:

$$0.058 \log \frac{[Fe^{+++}]}{[Fe^{++}]} = \frac{0.058}{2} 2 \log \frac{[Fe^{+++}]}{[Fe^{++}]} = \frac{0.058}{2} \log \frac{[Fe^{+++}]^2}{[Fe^{++}]^2}$$

Now the coefficient $\frac{0.058}{2}$ in Eq. (3) can be taken outside the brackets:

$$\frac{0.058}{2} \left(\log \frac{[Sn^{++++}]}{[Sn^{++}]} - \log \frac{[Fe^{+++}]^2}{[Fe^{++}]^2} \right) = 0.77 - 0.15$$

and hence

$$\log \frac{[Sn^{++++}] \cdot [Fe^{++}]^2}{[Sn^{++}] \cdot [Fe^{+++}]^2} = \frac{(0.77 - 0.15) \cdot 2}{0.058}$$

Since the expression after the logarithm sign is the equilibrium constant of the reaction, we can write:

$$\log K = \frac{(0.77 - 0.15) \cdot 2}{0.058} \approx 21$$

which gives $K \approx 1 \times 10^{21}$.

This result shows that at equilibrium the product of the Sn^{++++} and Fe^{++} concentrations is about 1×10^{21} times the product of the concentrations of the remaining Sn^{++} and Fe^{+++} ions. This means that the reaction proceeds in the direction of Sn^{++++} and Fe^{++} formation from Sn^{++} and Fe^{+++}, and goes practically to completion.

In general, the relationship between the equilibrium constant of a reaction and the corresponding standard oxidation potentials (at 18°) may be represented by the equation

$$\log K = \frac{(E_0' - E_0'') \cdot n}{0.058} \qquad (4)$$

Here E_0' and E_0'' are the standard oxidation potentials of the couples corresponding to the oxidizing agent (E_0') and reducing agent (E_0'') taken.

If $E_0' > E_0''$, then $\log K > 0$ and $K > 1$. This means that at equilibrium the product of the concentrations of the substances formed in the reaction is greater than the product of the residual original substances. In other words, the reaction proceeds in the direction indicated and, if the difference $E_0' - E_0''$ is large enough, it goes practically to completion. Conversely, if $E_0' < E_0''$ (i.e., if the oxidizing agent used is less active than the one we expect to be formed in the reaction), K is very small when the difference of the potentials is large. This means that the equilibrium is shifted far to the left, and the reverse reaction goes almost to completion.

Thus, Eq. (4) confirms the rule according to which the reaction should yield an oxidizing and a reducing agent which are weaker than the ones taken; never the reverse*.

If the difference between the oxidation potentials of the two couples is small, the equilibrium constant should be close to unity and the reaction does not go to completion unless the conditions are adjusted to shift the equilibrium to the desired direction. For example, the equilibrium constant of the reaction

$$AsO_4^{---} + 2I^- + 2H^+ \rightleftarrows AsO_3^{---} + I_2 + H_2O$$

(in accordance with a difference of 0.03 V between the oxidation potentials) is only about 10. Therefore, if we require practically complete conversion of the original substances we must increase the H^+ ion concentration by addition of concentrated HCl to the solution. Increase of the I^- ion concentration also shifts the equilibrium; this is evident from the equation

$$K = \frac{[AsO_3^{---}] \cdot [I_2]}{[AsO_4^{---}] \cdot [I^-]^2 \cdot [H^+]^2} \approx 10$$

It should be noted that the table of oxidation potentials makes it possible to estimate equilibrium constants, but *it gives no information about the rate at which equilibrium is reached.*

Experiments show that sometimes a larger difference of potentials corresponds to a lower rather than a higher reaction rate. For example, the oxidation of hydrogen by oxygen, a reaction with a difference of potentials of 1.23 V, proceeds at an immeasurably low rate at room temperature (to which Table 20 refers). On the other hand, the oxidation of Fe^{++} to Fe^{+++} by oxygen is much more rapid although the difference of potentials is less (0.46 V).

---

* If, of course, the reaction is not reversed owing to a change of concentration.

Slow reactions can be accelerated by various methods. The first of these to be noted is increase of temperature; the rate of a reaction is increased on the average two- to three-fold by a temperature rise of 10°. Thus, reaction rates increase in geometrical progression as the temperature rises in arithmetical progression.

Another factor influencing reaction rates is the concentration of the reacting substances. It was explained earlier (see Sec. 9) that by the law of mass action the reaction rate in a homogeneous medium is directly proportional to the product of the concentrations of the reactants, if these concentrations are raised to the powers corresponding to their stoichiometric coefficients. Thus, the rate of the reaction

$$2I^- + H_2O_2 + 2H^+ = I_2 + 2H_2O$$

should be, by the law of mass action,

$$v = K\,[I^-]^2 \cdot [H_2O_2] \cdot [H^+]^2$$

If we take

$$[I^-] = [H_2O_2] = [H^+] = c$$

we obtain

$$v = K \cdot c^5$$

However, experiment shows that the rate of this reaction is proportional to the square of the concentration, i.e., $v = Kc^2$, and not to the fifth power as indicated by the law of mass action. Many other oxidation-reduction processes show similar deviations from the law of mass action.

The cause of these deviations is the complex course of oxidation-reduction reactions, which usually pass through a series of intermediate stages, so that the equations are merely additive without reflecting the true course of the process. The rates of such complex reactions depend on the rates of their individual stages and therefore cannot be predicted from the overall reaction equations.

The following reasoning shows that many oxidation-reduction processes must pass through a series of intermediate stages. A chemical reaction in solution occurs as the result of collisions between the reacting ions or molecules. Under given conditions the probability of a collision depends on the number of different ions (or molecules) involved in the given reaction. In the case of what are known as termolecular reactions, which require simultaneous collisions of three particles at single points in space, and in the exact proportions demanded by the reaction equation, e.g.,

$$Sn^{++} + 2Fe^{+++} = Sn^{++++} + 2Fe^{++}$$

the probability of collision must evidently be much less than in the case of bimolecular reactions. which involve the collisions of only

two particles, e.g.,

$$Ce^{++++} + Fe^{++} = Ce^{+++} + Fe^{+++}$$

Reactions requiring simultaneous collisions of four, five, or more particles are so improbable that they may be regarded as virtually impossible. Nevertheless, very many oxidation-reduction reactions are represented by equations with large coefficients and appear to require collisions between large numbers of particles at single points in space (for example, 5 particles for the reaction between I^- ions and H_2O_2, 14 for the reaction between Fe^{++} and MnO_4^- ions in acid solution, etc.). It is obvious that these are overall equations; in reality any such reaction passes through a series of intermediate stages each of which is a bimolecular or termolecular reaction.

In many cases the nature of these intermediate stages is not known. In certain instances some of them have been identified so that the true course of the process can be established. For example, it has been shown experimentally for the reaction

$$2I^- + H_2O_2 + 2H^+ = I_2 + 2H_2O \qquad (5)$$

that one of the intermediate stages is the formation of hypoiodous acid, HIO:

$$I^- + H_2O_2 = IO^- + H_2O \qquad (6)$$

$$IO^- + H^+ = HIO \qquad (7)$$

The HIO formed, which is an active oxidizing agent, oxidizes I^- ions:

$$HIO + I^- + H^+ = I_2 + H_2O \qquad (8)$$

Adding Eqs. (6), (7) and (8) together, we obtain the overall reaction equation (5).

If a reaction proceeds by a number of intermediate stages, *its rate must be determined by the rate of the slowest reaction.* In this instance the slowest step is reaction (6), i.e.,

$$I^- + H_2O_2 = IO^- + H_2O$$

Since this is a bimolecular reaction, its rate and therefore the rate of the whole oxidation-reduction process, represented by the overall equation

$$2I^- + H_2O_2 + 2H^+ = I_2 + 2H_2O$$

must be proportional to the square of the concentration; this is confirmed experimentally.

One interesting and frequently observed feature, which is of great significance, clearly stands out in this reaction: whereas the final result of the overall reaction is oxidation of I^- ions to I_2, i.e., to an increase of the valency of iodine from —1 to 0, at the initial stages [see Eqs. (6) and (7)] its valency increases from —1 to +1 (in the

IO^- ion and HIO). Thus, an intermediate product is formed with iodine in a higher state of oxidation (HIO) than in the final state of the system (I_2). This intermediate compound in a higher oxidation state, being a powerful oxidizing agent, oxidizes the yet unconverted reducing agent (I^- ions) and is itself reduced to free I_2. Such a course of oxidation-reduction processes, with formation of unstable intermediate compounds in higher oxidation states (described as "primary oxides"), has been established in many instances.

Thus, in the reaction between Fe^{++} and MnO_4^- ions in acid solution a very unstable intermediate compound of quinquevalent iron (primary oxide) is apparently formed first. This reaction can be represented schematically as follows:

$$5Fe^{++} + 3Mn^{+VII} = 3Mn^{++} + 5Fe^{+V}$$

The primary oxide, having high oxidizing activity, immediately reacts with yet unconverted Fe^{++} ions and oxidizes them to Fe^{+++}:

$$Fe^{+V} + 2Fe^{++} = 3Fe^{+++}$$

As the result of these reactions all the Fe^{++} ions are oxidized to Fe^{+++}.

The formation of primary oxides in oxidation-reduction reactions explains *coupled oxidation*. It has been found that one oxidation-reduction process may induce some other oxidation-reduction reaction which would not occur by itself under the given conditions. For example, when dilute $KMnO_4$ solution is added in the cold to a dilute solution of a ferrous salt containing HCl (or chlorides), the permanganate oxidizes the Cl^- ions to Cl_2 in addition to oxidizing Fe^{++} to Fe^{+++}. However, in the absence of Fe^{++} permanganate does not oxidize Cl^- ions under these conditions. Thus, the reaction

$$5Fe^{++} + MnO_4^- + 8H^+ = 5Fe^{+++} + Mn^{++} + 4H_2O$$

induces the coupled reaction

$$10Cl^- + 2MnO_4^- + 16H^+ = 5Cl_2 + 2Mn^{++} + 8H_2O$$

The explanation is that, as we have seen, a primary oxide is formed in the reaction between Fe^{++} and permanganate, and this primary oxide oxidizes Cl^- as well as Fe^{++} ions:

$$Fe^{+V} + 2Cl^- = Fe^{+++} + Cl_2$$

The theory of primary oxide formation in oxidation-reduction reactions was put forward by the eminent Russian chemist A. N. Bakh. Detailed investigations of coupled oxidation-reduction reactions were carried out by Prof. N. A. Shilov (1901-1904).

The intermediate stages in oxidation-reduction reactions account for the catalytic acceleration of these reactions by certain substances

(or ions) in a homogeneous medium. *A catalyst is defined as a substance which alters the rate of a reaction without itself being expended in the reaction.* Most of the catalysts met in practice accelerate reactions, but catalysts which lower reaction rates are also known. The fact that a catalyst is not consumed in a reaction does not necessarily mean that it takes no part in the reaction. The catalyst is usually involved in the intermediate stages of a reaction and is not expended only because it is fully regenerated at later reaction stages after having been consumed at an earlier stage. It follows that the stages through which a reaction passes are different in the presence of a catalyst. If the rates of these new stages are higher, the reaction is accelerated.

Let us consider a reaction studied by N. A. Shilov, which is of great importance in quantitative analysis; this is the reaction between permanganate and oxalic acid:

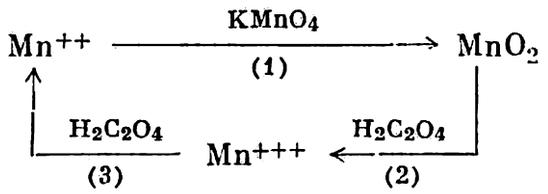
$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

or

$$5C_2O_4^{--} + 2MnO_4^- + 16H^+ = 10CO_2 + 2Mn^{++} + 8H_2O$$

It is found that if $KMnO_4$ solution is added drop by drop to an acidified solution of $H_2C_2O_4$ warmed to 70-80°, the decolourization (i.e., reduction of MnO_4^- ions to Mn^{++}) of the first few drops is slow. If a small amount of $MnSO_4$ is added to the solution, the decolourization of permanganate is practically instantaneous. The $MnSO_4$ is not itself consumed in the reaction, but accelerates it catalytically.

According to Shilov, the accelerating effect of Mn^{++} ions can be explained as follows. The added Mn^{++} ions are oxidized by permanganate to manganese dioxide, MnO_2. The latter is expended for oxidation of $H_2C_2O_4$ as soon as it is formed. The oxidation apparently proceeds in two stages: MnO_2 is first reduced to Mn^{+++}, which reacts with more $H_2C_2O_4$ and is thereby reduced further to Mn^{++}. The latter is thus fully regenerated. All this can be represented schematically as follows:



The reaction stages given in the scheme can be represented by the following equations:

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4 \quad (9)$$

$$2MnO_2 + H_2C_2O_4 + 3H_2SO_4 = Mn_2(SO_4)_3 + 4H_2O + 2CO_2 \quad (10)$$

$$Mn_2(SO_4)_3 + H_2C_2O_4 = 2MnSO_4 + H_2SO_4 + 2CO_2 \quad (11)$$

If we multiply Eq. (9) by 2, and Eqs. (10) and (11) by 5 and add all three together, we obtain the overall equation given above. This shows that the added $MnSO_4$ is fully regenerated during the reaction.

As the occurrence of reactions involving more than three interacting particles in the equation is highly improbable, it seems likely that each of the intermediate reactions discussed above must itself pass through certain intermediate stages. However, the nature of these stages is as yet unknown.

The equation

$$5C_2O_4^{--} + 2MnO_4^- + 16H^+ = 10CO_2 + 2Mn^{++} + 8H_2O$$

shows that Mn^{++} ions, which accelerate the reaction, are formed. Such reactions are known as *autocatalytic*. It is evident that the rate of this reaction, very low at the initial instant becomes very high as soon as a certain amount of Mn^{++} has been formed, and falls again only near the end, when the $C_2O_4^{--}$ ion concentration has become very low.

QUESTIONS AND PROBLEMS

1. What are the consequences of strength differences between various oxidizing or reducing agents?
2. Explain how the conditions for an oxidation-reduction reaction in a galvanic cell differ from the conditions without a cell.
3. Explain the chemical processes taking place at the positive and negative poles of any galvanic cell.
4. Describe the arrangement of a standard hydrogen electrode.
5. What are standard oxidation potentials and how are they determined? Explain how the relative strengths of oxidizing and reducing agents can be deduced from standard oxidation potentials.
6. The standard oxidation potential of the Mn^{++}/Mn couple is —1.10 V. Describe the processes taking place in a cell composed of this pair and a standard hydrogen electrode. Write the overall equation for the reaction.
7. Repeat the answers to Q.6 for a cell composed of the Sb^{+++}/Sb couple (see Table VIII in Appendix) and a standard hydrogen electrode.
8. Calculate the oxidation potential of Mn^{++}/Mn at Mn^{++} concentrations of (a) 2 g-ion/litre; (b) 0.005 g-ion/litre.

Answer. (a) $E = -1.091$ V; (b) $E = -1.167$ V.

9. A cell consisting of a standard hydrogen electrode and a Ni^{++}/Ni electrode with a Ni^{++} ion concentration of 0.01 g-ion/litre has an emf of 0.288 V, and the nickel electrode is the negative pole. Calculate the standard oxidation potential of Ni^{++}/Ni.

Answer. $E_0 = -0.230$ V.

10. Calculate the oxidation potentials of (a) the Sn^{++++}/Sn^{++} couple for $[Sn^{++++}] = 0.001$ g-ion/litre and $[Sn^{++}] = 0.1$ g-ion/litre; (b) the MnO_4^-/Mn^{++} couple for equal concentrations of the oxidized and reduced forms at pH = 5.

Answer. (a) 0.092 V; (b) 1.046 V.

11. Find the emf of a cell consisting of Sn^{++++}/Sn^{++} and Fe^{+++}/Fe^{++}, if the Sn^{++++} and Fe^{++} concentrations are both 0.01 g-ion/litre and the Sn^{++} and Fe^{+++} concentrations are both 1 g-ion/litre.

Answer. 0.794 V.

12. Can metallic lead displace copper from solutions of copper salts? Can iron be displaced by metallic copper from $FeSO_4$ solution?

13. Of the metals Sn, Cu, Al and Hg, which can displace hydrogen from acids?

14. State which of the following oxidations can be effected by the action of $K_2Cr_2O_7$ in acid solution: (a) Fe^{++} to Fe^{+++}; (b) AsO_3^{---} to AsO_4^{---}; (c) Mn^{++} to MnO_4^-; (d) SO_3^{--} to SO_4^{--}; (e) SO_4^{--} to $S_2O_8^{--}$.

15. Can the following reductions be effected by means of Sn^{++} ions: (a) Br_2 to Br^-; (b) Fe^{+++} to metallic iron; (c) Fe^{+++} to Fe^{++} ions?

16. State what happens when (a) metallic iron is added to an acidified solution containing Cu^{++} and Cd^{++} ions; (b) metallic aluminium is added to an acidified $Fe_2(SO_4)_3$ solution.

17. Explain why the action of HCl or H_2SO_4 on metallic iron yields ferrous salts, while HNO_3 gives ferric salts.

18. Hydrogen sulphide is passed through an acid solution containing MnO_4^-, $Cr_2O_7^{--}$, and Fe^{+++} ions. What processes take place, and in what sequence?

19. An equivalent amount of HCl is added to $AgNO_3$ solution which is one of the electrolytes in a cell consisting of the Ag^+/Ag couple and a standard hydrogen electrode. Does this addition reverse the direction of the current in the cell?

Answer. No.

20. To 0.1 *M* $AgNO_3$ solution, which is one of the electrolytes in the cell of Q.19, enough solid KCN is added to a CN^- ion concentration of 1 g-ion/litre. Using the instability constant of the $[Ag(CN)_2]^-$ complex (see Table V in Appendix), calculate whether the direction of the current is reversed.

Answer. Yes.

21. Use the table of standard oxidation potentials to determine whether manganese dioxide, MnO_2, can oxidize hydrochloric acid to chlorine. Explain why it is possible to prepare Cl_2 by the action of concentrated HCl on MnO_2. State how increase of HCl concentration influences the oxidation potentials of both pairs involved in the reaction.

22. Derive the formulas for calculating the equilibrium constants of the reactions:

$$\text{(a) } Sn^{++} + I_2 \rightleftarrows Sn^{++++} + 2I^-$$

$$\text{(b) } MnO_4^- + 8H^+ + 5Fe^{++} \rightleftarrows Mn^{++} + 5Fe^{+++} + 4H_2O$$

and find the numerical values of the constants. In which of these reactions is the conversion of the starting substances more complete?

Answer. (a) $\log K = 13.45$; $K = 2.8 \times 10^{13}$; (b) $\log K = 63.8$; $K = 6.3 \times 10^{63}$.

23. In what cases does the solution pH influence the direction of oxidation-reduction reactions? Illustrate your answer by examples.

24. State in what cases (a) an acid solution and (b) an alkaline solution is required for oxidation-reduction reactions to take place.

REACTIONS AND ANALYTICAL PROCEDURE FOR GROUP IV CATIONS

65. General Characteristics of Group IV Cations

Group IV cations include Ag^+, Pb^{++}, Hg_2^{++}, Hg^{++}, Cu^{++}, Cd^{++} and Bi^{+++}. *Their sulphides have much lower solubility products than the sulphides of Group III.* The solubility products of the sulphides are so low that they are greatly exceeded not only by the action of

$(NH_4)_2S$ but also by the action of hydrogen sulphide, which has a much lower S^{--} ion concentration in solution. The solubility product is exceeded even if an acid is present in solution, as the hydrogen ions from the acid suppress the already slight dissociation of H_2S. Since the S^{--} and H^+ ion concentrations are connected by the equation (see Sec. 39):

$$[H^+]^2 \cdot [S^{--}] = 6.8 \times 10^{-24}$$

Group IV sulphides are precipitated even at relatively high H^+ ion concentrations.

Accordingly, *in contrast to Group III cations, Group IV cations are precipitated by* H_2S *as well as by* $(NH_4)_2S$, *from alkaline, neutral or acid solutions of their salts.*

For complete precipitation the pH must be not less than 0.5, corresponding to an H^+ ion concentration of 0.3 g-ion/litre (Sec. 39). For the same reason the Group IV sulphides are insoluble in dilute acids, except HNO_3 on heating (distinction from Group III). All these facts, important in analysis, are discussed in detail in Sections 39 and 40.

The Group IV reagent is H_2S in acid solution*.

Group IV is subdivided into two subgroups in accordance with the different solubilities of the chlorides.

(a) *The first (silver) subgroup* comprises Ag^+, Pb^{++} and Hg_2^{++} ions, the chlorides of which are sparingly soluble and are precipitated by HCl.

(b) *The second (copper) subgroup* comprises Cu^{++}, Hg^{++}, Cd^{++} and Bi^{+++} cations, which form water-soluble chlorides which are not precipitated by HCl.

The metals forming the Group IV cations are in the second half of the fourth, fifth and sixth long periods of Groups I (Cu and Ag), II (Cd and Hg), IV (Pb) and V (Bi) of the Mendeleyev periodic system. The cations of these elements have either complete outer shells of 18 electrons or shells containing 18 + 2 electrons in the two outer layers. The exception is the Cu^{++} cation, which has an incomplete outer shell (see Table 3, p. 34).

There is a direct connection between the structure of the outer electron shells and the properties of the sulphides formed by the cations. It is known that cations with multielectron outer layers are strong polarizers and are themselves easily polarized. This is especially prominent for cations with 18 and 18 + 2 outer electron structures.

When such cations react with easily deformed S^{--} ions, both ions are strongly polarized and their outer electron shells undergo considerable deformation.

As a result, the bonds between the atoms (ions) approximate to covalent in type. Accordingly, all cations with 18 or 18 + 2 outer electron structures

* In acid solution, hydrogen sulphide precipitates Group V ions together with the Group IV cations (see Sec. 75).

as a general rule form sulphides with very small solubility products and therefore belong to analytical Groups IV and V.

In contrast, cations with complete outer layers of 2 and 8 electrons are weak polarizers and are polarized very little themselves. When such cations react with S^{--} anions the electron shells do not undergo appreciable deformation. Such cations, as a general rule, do not form sparingly soluble sulphides and belong to analytical Groups I and II. Those Group III cations which, like Al^{+++}, are precipitated by ammonium sulphide in the form of their hydroxides also belong here.

Cations with a transitional electron structure, i.e., with incomplete 18-electron outer layers, occupy an intermediate position. They are relatively strong polarizers and are themselves polarized to an appreciable extent; therefore they yield sparingly soluble sulphides by reacting with S^{--} ions. However, these sulphides vary considerably in solubility in accordance with the positions of the respective elements in the periodic system. Cations formed from elements of the second and third triads of the Mendeleyev system, Ru^{+++}, Rh^{+++}, Pd^{++}, Os^{++++}, Ir^{++++}, Pt^{++++}, like cations with 18 and 18 + 2 electron structures, belong to analytical Groups IV and V. The reason is that the presence of inner layers of 18 and 32 electrons intensifies their polarizing power and polarizability, while intensification of polarization interactions when cations combine with S^{--} ions leads to decreased solubility of the corresponding sulphides.

Cations formed from elements of the first triad of the periodic system, Fe^{++}, Co^{++}, Ni^{++}, and the adjacent Mn^{++} cations, do not have inner layers of 18 or 32 electrons; their polarizing power and polarizability are relatively low. Accordingly, their sulphides, although sparingly soluble, have considerably larger solubility products than the cations of Groups IV and V, and therefore belong to analytical Group III.

The foregoing comments on the significance of the external electron structures are illustrated by Table 21.

Silver, which has only one salt-forming oxide, is always present in solution as the univalent Ag^+ ion. Similarly, lead, cadmium and bismuth each yield only one cation of practical significance in solution, namely Pb^{++}, Cd^{++} and Bi^{+++}. On the other hand, mercury and copper both form two series of ions; Hg_2^{++} and Cu^+ in -ous salts, and Hg^{++} and Cu^{++} in —ic salts.

The Hg_2^{++} cation, which forms the sparingly soluble chloride Hg_2Cl_2, belongs to the first subgroup of Group IV. The Hg^{++} cation is intermediate in properties between Groups IV and V and can be allocated to either group in accordance with the method used for separating the groups. With the separation method adopted in this book, the Hg^{++} cation belongs to the second subgroup of Group IV.

The Cu^+ cation is not considered here, as it is very unstable and is of secondary importance in comparison with Cu^{++}.

The hydroxides of these cations (with the exception of silver), like those of Group III, are very weak bases, so that their salts are highly hydrolyzed and yield acidic solution.

Most of the Group IV cations have a tendency to form complexes with ammonia, cyanides, and other substances. Only the Pb^{++} and Bi^{+++} cations do not form ammine complexes.

Table 21

Electronic Structures of Cations and Analytical Groups

Electronic structure	Cations	Analytical groups
Complete 2- and 8-electron outer layers	Li^+, K^+, Na^+, Rb^+, Cs^+, Fr^+, (Mg^{++}) Ca^{++}, Sr^{++}, Ba^{++} Ra^{++}	I and II
	Be^{++}, Mg^{++}, Al^{+++}, Sc^{+++}, Y^{+++}, La^{+++}, lanthanide ions M^{+++}, Ac^{+++}, actinide ions M^{+++}, M^{++++}, Ti^{+++}, Zr^{++++}, Hf^{+++}, Nb^V, Ta^V (Cr^{+++})	III [subgroup A, precipitated by $(NH_4)_2S$ as hydroxides]
Incomplete outer layer of 18 electrons	V^{IV}, Cr^{+++}, Mn^{++}, Fe^{++}, Fe^{+++}, Co^{++}, Ni^{++} (Zn^{++}, In^{+++}, Ga^{+++})	III [subgroup B, precipitated by $(NH_4)_2S$ as sulphides]
	Cu^{++}, Ru^{+++}, Rh^{+++}, Pd^{++}, Os^{IV}, Ir^{IV}, Pt^{IV}	IV and V
Complete outer layer of 18 electrons	Cu^+, Ag^+, Au^+, Zn^{++}, Cd^{++}, Hg^{++}, Ga^{+++}, In^{+++}, Ge^{IV}, Sn^{IV}, Sb^V, As^V	IV and V
Outer electronic structure 18+2	Tl^+, Sn^{++}, Pb^{++}, As^{III}, Sb^{III}, Bi^{+++}	

66. Action of the Group Reagents

Let us consider the action of the group reagent (H_2S) and of the reagent which precipitates the first subgroup (HCl).

1. Action of H_2S. Hydrogen sulphide is usually obtained in the laboratory by the action of hydrochloric acid on ferrous sulphide:

$$FeS + 2HCl = FeCl_2 + H_2S \uparrow$$

Since this reaction does not require heat, it is conducted in a Kipp's apparatus (Fig. 36,*1*) or in automatic apparatus of similar type. It should be remembered that the liberated H_2S can carry with it droplets of liquid containing the ferrous salt $FeCl_2$ formed in the reaction. To avoid contamination by this salt, the gas is first purified by passage through a wash bottle *2* containing water.

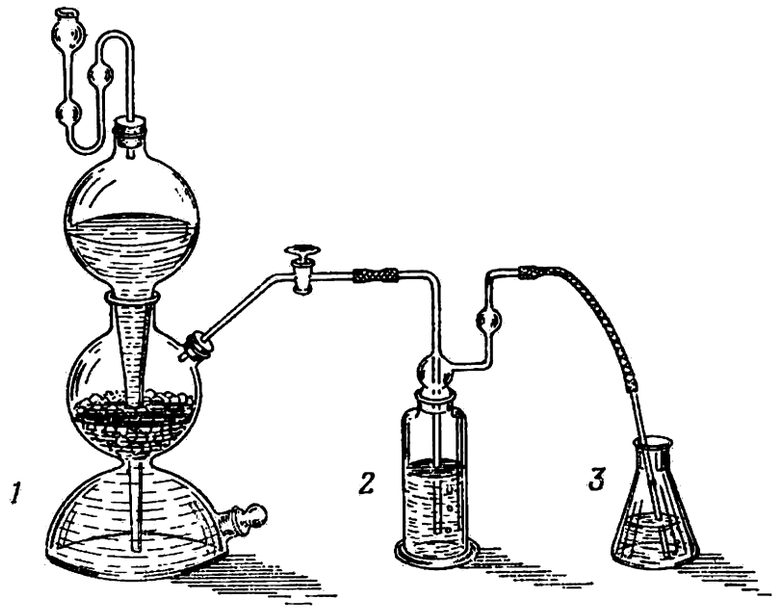


Fig. 36. Precipitation by hydrogen sulphide
1—Kipp's apparatus; *2*—wash bottle; *3*—flask with solution for analysis

The wash bottle is fitted with a rubber tube to which a thoroughly washed glass tube should be attached. This glass tube is immersed in the flask *3* with the solution for analysis.

Remember that *all operations with sulphides and* H_2S *must be performed in a fume cupboard in a special "hydrogen sulphide" room.* Very serious poisoning may occur if this rule is not obeyed.

It should not be forgotten that in precipitation by hydrogen sulphide only the dissolved part of the gas plays an active part. Accordingly, the stream of H_2S must be so slow that the bubbles in the wash bottle *2* can be easily counted. Otherwise the main bulk of the hydrogen sulphide passes uselessly through the solution and contaminates the air. *Having finished work with the hydrogen sulphide generator, do not forget to close the tap.*

Remembering all these instructions, study the action of H_2S on Group IV cations experimentally.

When H_2S acts on solutions of silver, lead, mercury, copper and bismuth salts, black precipitates of Ag_2S, PbS, HgS, CuS and Bi_2S_3

are formed; for example*

$$2Ag^+ + H_2S = \downarrow Ag_2S + 2H^+$$

$$Cu^{++} + H_2S = \downarrow CuS + 2H^+$$

$$2Bi^{+++} + 3H_2S = \downarrow Bi_2S_3 + 6H^+$$

Solutions of cadmium salts give a characteristic bright yellow precipitate of CdS, the formation of which is the most important qualitative test for the Cd^{++} ion:

$$Cd^{++} + H_2S = \downarrow CdS + 2H^+$$

The Hg_2^{++} ion gives a precipitate of Hg_2S, which immediately decomposes into HgS and Hg:

$$Hg_2(NO_3)_2 + H_2S = \downarrow Hg_2S + 2HNO_3$$

$$Hg_2S = HgS + Hg$$

The equation in the ionic form is

$$Hg_2^{++} + H_2S = \downarrow HgS + \downarrow Hg + 2H^+$$

The resultant mixture of HgS and Hg is black.

In contrast to Group III sulphides, the sulphides of Group IV are insoluble in dilute acids (HCl, H_2SO_4), because their solubility products are so small that there is virtually no reaction between H^+ ions and the S^{--} ions which they yield in solution (Sec. 40). However, they dissolve readily in dilute HNO_3, which oxidizes S^{--} ions to free sulphur, e.g.,

$$3CuS + 8HNO_3 = 3Cu(NO_3)_2 + \downarrow 3S + 2NO\uparrow + 4H_2O$$

or

$$3CuS + 2NO_3^- + 8H^+ = 3Cu^{++} + \downarrow 3S + 2NO\uparrow + 4H_2O$$

This reaction should be carried out with heating. It is helpful to add a little KNO_2 or $NaNO_2$ to accelerate the reaction. Nitrogen oxides are formed, which catalyze the reaction.

One of the most soluble of the Group IV sulphides, CdS ($SP = 3.6 \times \times 10^{-29}$), dissolves in sufficiently concentrated HCl solutions as well as in HNO_3. For example, 1 *N* HCl dissolves a considerable amount of CdS on heating; this may be used for separating Cd^{++} from Cu^{++} when the colour of cadmium sulphide is masked by simultaneous pre-

* In the case of Pb^{++} and Hg^{++} a red ($PbCl_2 \cdot PbS$) or white ($HgCl_2 \cdot 2HgS$) precipitate may form first. However, further treatment with H_2S converts them into black PbS and HgS precipitates.

cipitation of other sulphides, such as CuS or Bi_2S_3. Because of the appreciable solubility of CdS, the concentration of HCl must be kept low during separation of Group IV (see below).

The solubility of CdS in HCl is due not only to combination of S^{--} ions with H^+ ions from the acid but also to the formation of the complex $[CdCl_4]^{--}$, which results in a considerable decrease of the Cd^{++} ion concentration. This is confirmed by the fact that CdS is not precipitated from a moderately acid solution (pH $\approx$ 0.5) if NH_4Cl is added prior to saturation. The behaviour of the Cd^{++} ion with H_2S in the presence of HCl at 1 *N* concentration (or higher) or with ammonium chloride can be used for separating cadmium from copper, which occur together in the analysis.

It is also clear that this behaviour must be taken into account during separation of Group IV cations from Groups III, II and I. Great care must be taken that the pH of the solution during precipitation by hydrogen sulphide is not less than 0.5, otherwise the Cd^{++} ion may remain completely in solution and thus be "missed".

The above example also demonstrates the complications which may arise during analysis owing to the complex-forming action of Cl^- ions; this is one of the disadvantages of the hydrogen sulphide method of analysis.

In contrast to CdS, the least soluble of the sulphides under consideration, mercuric sulphide ($SP = 4 \times 10^{-53}$) is insoluble both in HCl and in HNO_3. It has to be dissolved in a stronger oxidizing agent, aqua regia (a mixture of 1 volume of concentrated HNO_3 and 3 volumes of concentrated HCl) on heating:

$$3HgS + 2HNO_3 + 6HCl = 3HgCl_2 + \downarrow 3S + 4H_2O + 2NO \uparrow$$

However, HgS can be dissolved in HCl if KI solution is added to bind the Hg^{++} ions in a very stable complex, $[HgI_4]^{--}$ ($K_{inst} = 5 \times \times 10^{-31}$). This reaction, which takes place on heating, is represented by the equation

$$HgS + 2HCl + 4KI = K_2[HgI_4] + 2KCl + H_2S \uparrow$$

Conditions for Precipitation of Group IV Cations by Hydrogen Sulphide. (a) As stated in Sec. 39, Group IV cations must be precipitated in acid solution; otherwise the solubility product of zinc sulphide (1.2×10^{-23}) is exceeded and ZnS is precipitated. However, the solution must not be too acid, because in that case the precipitation of CdS ($SP = 3.6 \times 10^{-29}$) is not complete. Sometimes the Cd^{++} ions may even remain completely in solution. The most suitable H^+ ion concentration for precipitation of Group IV cations by hydrogen sulphide is about 0.3 g-ion/litre.

Another complication in adjusting the pH in this case is the fact that there is no known suitable buffer mixture for pH = 0.5.

Therefore the acid present in the solution must first be neutralized (because it is not known how much is present), and 2 *N* HCl solution must then be added in an amount corresponding to 1/5 of the solution volume. This makes the HCl concentration (and therefore the H^+ ion concentration) about 0.3 *M*, corresponding to pH $\approx$ 0.5.

In this case the pH cannot be determined by means of an appropriate indicator (such as methyl violet, which has a range of pH = 0-2). This is because strongly acidic solutions have a considerable buffering action (p. 73), i.e., they change pH very slowly. For example, to lower the pH of a solution from 1 to 0 we must add about 0.9 mole of HCl to a litre of solution. The precision of the pH measurement used is within one pH unit. It is evident, therefore, that we cannot achieve the required precision in pH adjustment by this method. Of course, the pH can be determined more accurately by comparing the colour of methyl violet under the action of this solution with the colour given by the indicator with 0.3 *N* HCl under the same conditions, but this method is less reliable than the one recommended above, and some skill is needed in using it.

(b) Before H_2S is passed, it is preferable to acidify the solution with hydrochloric acid. If we used H_2SO_4, we would introduce SO_4^{--} ions, which precipitate Ba^{++}, Sr^{++} (Ca^{++}) and Pb^{++} as acid-insoluble sulphates and thereby complicate the analysis. Nitric acid is unsuitable because of its oxidizing action, which may lead to oxidation of S^{--} ions to free sulphur, especially at high HNO_3 concentrations. Finally, acetic acid is a weak acid and would not give a high enough H^+ ion concentration to prevent precipitation of zinc sulphide. However, HCl also suffers from a disadvantage because of the tendency of Cl^- to form complexes with a number of cations, thus lowering their concentration.

Since Group IV is precipitated in the presence of HCl, its first subgroup is precipitated as chlorides even before the action of H_2S and is therefore separated from the other cations. The chloride precipitate is analyzed separately.

(c) The precipitation should be performed in a hot solution to avoid the formation of colloidal sulphide solutions. However, H_2S (like all other gases) becomes less soluble at higher temperatures and as a result the separation of Group IV cations is less complete. Therefore at the end of the precipitation the solution is diluted with an equal volume of cold distilled water and again saturated with H_2S. This not only cools the solution but also lowers the H^+ ion concentration, thus making the precipitation of Cd^{++} more complete.

(d) When precipitated Group IV sulphides are left to stand in contact with the solution, "delayed precipitation" of zinc sulphide takes place (p. 197). Therefore filtration should not be delayed too long, in order to avoid "loss" of Zn^{++}.

2. Action of HCl. Dilute hydrochloric acid (and solutions of chlorides) precipitates Ag^+, Hg_2^{++} and Pb^{++} as the white compounds

AgCl, Hg_2Cl_2 and $PbCl_2$, e.g.,

$$Ag^+ + Cl^- = \downarrow AgCl$$

$$Hg_2^{++} + 2Cl^- = \downarrow Hg_2Cl_2$$

Prepare all three chlorides and study their properties.

(a) The AgCl precipitate coagulates into white curdy flakes when the test tube is shaken. It becomes violet or even black (owing to decomposition) when exposed to light. Silver chloride, being a salt of a strong acid, is not soluble in dilute acids (HNO_3, H_2SO_4). It is readily soluble in NH_4OH because Ag^+ ions (present in solution from the precipitate) form complex $[Ag(NH_3)_2]^+$ ions:

$$AgCl + 2NH_4OH \rightleftarrows [Ag(NH_3)_2]Cl + 2H_2O$$

If an acid, such as HNO_3, is added to the resultant solution of $[Ag(NH_3)_2]Cl$ the hydrogen ions of the acid combine with NH_3 molecules to form the even more stable NH_4^+ complex and the $[Ag(NH_3)_2]^+$ dissociation equilibrium

$$[Ag(NH_3)_2]^+ \rightleftarrows Ag^+ + 2NH_3$$

is disturbed. This leads to decomposition of the ammoniacal silver complex and Ag^+ ions appear in the solution. However, as the solution also contains Cl^- ions, formed by the first-stage dissociation of $[Ag(NH_3)_2]Cl$, the solubility product of AgCl is exceeded and this salt is precipitated. The overall equation for the reaction is

$$[Ag(NH_3)_2]Cl + 2HNO_3 = \downarrow AgCl + 2NH_4NO_3$$

Separation of AgCl from Hg_2Cl_2 in analysis is effected by the action of NH_4OH, and Ag^+ is detected by the action of HNO_3 on the $[Ag(NH_3)_2]Cl$ solution formed. Another way of detecting Ag^+ is to use the fact that Ag^+ forms the highly insoluble salt AgI with I^- ions; the solubility product of this salt (1.5×10^{-16}) is very much less than the instability constant of the complex $[Ag(NH_3)_2]^+$ ($K_{inst} = 6.8 \times 10^{-8}$). Therefore, if KI is added to a solution of $[Ag(NH_3)_2]Cl$ the Ag^+ ion concentration is sufficient for the solubility product of AgI to be exceeded, and the latter is precipitated (Sec. 48). The equation is

$$[Ag(NH_3)_2]Cl + KI + 2H_2O = \downarrow AgI + KCl + 2NH_4OH$$

or

$$[Ag(NH_3)_2]^+ + I^- + 2H_2O = \downarrow AgI + 2NH_4OH$$

The colour of the AgI precipitate is yellow. It may dissolve in excess KI owing to formation of the complex salt $K[AgI_2]$.

The Ag^+ ion forms similar complexes with Cl^- ions as ligands. Therefore AgCl is appreciably soluble in fairly concentrated HCl and chloride solutions. The reaction with excess HCl is represented by the equation

$$AgCl + HCl = H[AgCl_2]$$

(b) The Hg_2Cl_2 precipitate is white. In contrast to AgCl, it does not dissolve in NH_4OH but turns black. In this case an amine derivative of univalent mercury is formed first:

$$Hg_2Cl_2 + 2NH_4OH = [NH_2Hg_2]Cl + NH_4Cl + 2H_2O$$

The composition of this substance corresponds to NH_4Cl in which two hydrogen atoms are replaced by two atoms of univalent mercury. However, it is unstable and decomposes as soon as it is formed:

$$[NH_2Hg_2]Cl = [NH_2Hg]Cl + Hg$$

The finely divided metallic mercury formed in this reaction is black; this accounts for the blackening of the precipitate.

This is a most important reaction of the Hg_2^{++} ion, which we shall use for its detection.

(c) The $PbCl_2$ precipitate is also white. It is soluble in hot water (test this). This fact is used for separating it from AgCl and Hg_2Cl_2. Lead chloride is also appreciably soluble even in cold water (11 g/litre at room temperature). Therefore Pb^{++} ions are not precipitated completely by HCl; the part remaining in solution is subsequently precipitated as PbS together with the cations of the second subgroup of Group IV.

67. Reactions of the Ag^+ Cation

The Ag^+ cation is colourless in aqueous solutions.

1. Caustic alkalies, NaOH and KOH, give a brown precipitate of Ag_2O with Ag^+ ions; this is formed owing to decomposition of the unstable silver hydroxide initially formed:

$$2AgNO_3 + 2NaOH = 2AgOH + 2NaNO_3$$

$$2AgOH = \downarrow Ag_2O + H_2O$$

The precipitate is soluble in NH_4OH to form a complex silver ammine

$$Ag_2O + 4NH_4OH = 2[Ag(NH_3)_2]OH + 3H_2O$$

NH_4OH can also precipitate Ag_2O from solutions of silver salts, but the precipitate dissolves immediately in excess reagent.

2. Potassium chromate, K_2CrO_4, forms a brick-red precipitate of Ag_2CrO_4 with Ag^+:

$$2Ag^+ + CrO_4^{--} = \downarrow Ag_2CrO_4$$

The precipitate is soluble in HNO_3 and NH_4OH, but dissolves only with great difficulty in CH_3COOH.

3. Disodium hydrogen phosphate, Na_2HPO_4, gives a yellow precipitate of Ag_3PO_4, soluble in HNO_3 and NH_4OH, with Ag^+ ions:

$$3Ag^+ + 2HPO_4^{--} = \downarrow Ag_3PO_4 + H_2PO_4^-$$

If we compare this reaction with the analogous reactions of Ba^{++}, Ca^{++} and Sr^{++} ions, where the acid salts are precipitated, e.g.,

$$Ba^{++} + HPO_4^{--} = \downarrow BaHPO_4$$

the difference may appear strange at first sight. The reason lies in the different solubilities of the respective compounds. In the case of the silver salts, the least soluble is the neutral phosphate, Ag_3PO_4. Therefore, despite the low PO_4^{---} ion concentration in the Na_2HPO_4 solution*, the solibility product of Ag_3PO_4 is reached first, and this salt is precipitated**. On the other hand, in the case of barium, strontium and calcium salts the solubility products of the acid salts are reached first, and the latter are therefore formed.

4. Solutions of bromides and iodides (Br^- and I^- ions) precipitate pale yellowish AgBr and yellow AgI from solutions with Ag^+ ions:

$$Ag^+ + Br^- = \downarrow AgBr \quad (SP = 7.7 \times 10^{-13})$$

$$Ag^+ + I^- = \downarrow AgI \quad (SP = 1.5 \times 10^{-16})$$

In contrast to silver chloride ($SP = 1.56 \times 10^{-10}$), silver iodide is insoluble in NH_4OH (test this), while silver bromide dissolves in it only slightly. The reason for this different behaviour with NH_4OH lies in the different solubility products.

However, AgBr and AgI can be dissolved in KCN or $Na_2S_2O_3$ solutions, which form the complexes $[Ag(CN)_2]^-$ ($K_{inst} = 1 \times 10^{-21}$) and $[Ag(S_2O_3)]^-$ ($K_{inst} = 1 \times 10^{-13}$) which are less dissociated than $[Ag(NH_3)_2]^+$ ($K_{inst} = 6.8 \times 10^{-8}$)***.

5. Reduction of Ag^+ Ions to Metallic Silver. The standard oxidation potential of the Ag^+ ion is relatively high ($E_0 = 0.81$ V), and therefore various reducing agents can reduce it to metallic silver.

---

* The PO_4^{---} ion is formed by the subsequent very slight dissociation ($K_3 = 2.2 \times 10^{-13}$) of the HPO_4^{--} anion.

** It will be remembered that Na_2HPO_4 also precipitates the neutral salts of Group III cations.

*** AgI dissolves in $Na_2S_2O_3$ only if a large excess of the reagent is used.

a. Reduction by Formaldehyde, HCOH. Wash a test tube with chromic mixture and then with water to remove grease, put in a few drops of a silver salt solution, and dilute with 10 drops of water. Add 8-10 drops of 2 *N* NH_4OH solution and a few drops of dilute formaldehyde solution (formalin). When the tube is immersed in hot water, a bright mirror of metallic silver is formed on its walls:

$$Ag_2O + HCOH = \downarrow 2Ag + HCOOH$$

b. Reduction by Mn^{++} *Ions.* We have already used this reaction as a spot test for Mn^{++} (Sec. 56, 7).
The equation is

$$2AgCl + Mn^{++} + 4OH^- = \downarrow 2Ag + 2Cl^- + \downarrow MnO(OH)_2 + H_2O$$

This reaction can also be used as a spot test for Ag^+.

For this purpose it is modified as follows. A drop of the unknown solution is used instead of the silver salt solution, and Mn^{++} is introduced in a drop of $Mn(NO_3)_2$ solution. *Instantaneous blackening* of the spot by the action of alkali indicates the presence of Ag^+ ions*.

This test detects 2 μg of Ag^+. The dilution limit is 1 : 25,000.

6. **Microcrystalloscopic Test.** Put a small crystal of $K_2Cr_2O_7$ into a drop of the unknown solution acidified with acetic acid. Large red-brown or orange $Ag_2Cr_2O_7$ crystals are formed (see Fig. 30, p. 274). The detectable minimum is 0.15 μg, and the dilution limit is 1 : 6,600. Lead salts also form a precipitate with potassium dichromate. However, the $PbCrO_4$ crystals are easily distinguished from $Ag_2Cr_2O_7$, as the former are smaller and yellow rather than orange. Mercury salts interfere.

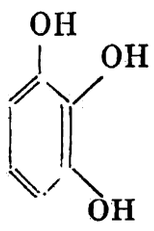
7. **Pyrogallol****, when ground with solid silver salts reduces them to metallic silver, and the mixture turns black. To study this test, evaporate 1-2 drops of $AgNO_3$ solution to dryness in a small basin, cool, and grind the dry residue with a few grains of solid pyrogallol.

Apart from mercury, the other Group IV cations do not interfere in this test for Ag^+. Mercury interferes only if it is present as the nitrate.

---

* Slow darkening is due to conversion of Mn^{++} into $MnO(OH)_2$ by the action of atmospheric oxygen.

** The formula of pyrogallol is



68. Reactions of the Pb^{++} Cation

The Pb^{++} ion is colourless in aqueous solutions.

1. Alkalies, NaOH, KOH, and NH_4OH, precipitate white $Pb(OH)_2$ which is soluble both in acids and in strong alkalies:

$$Pb(NO_3)_2 + 2NaOH = 2NaNO_3 + \downarrow Pb(OH)_2 \text{ (otherwise } H_2PbO_2)$$

$$H_2PbO_2 + 2NaOH = Na_2PbO_2 + 2H_2O$$

Na_2PbO_2 is sodium plumbite. The $Pb(OH)_2$ precipitate is insoluble in ammonia.

2. Sulphuric acid and soluble sulphates (SO_4^{--} ions) precipitate Pb^{++} in the form of white $PbSO_4$:

$$Pb^{++} + SO_4^{--} = \downarrow PbSO_4$$

The precipitate dissolves on heating in caustic alkali solutions owing to formation of plumbites, e.g.,

$$PbSO_4 + 4KOH = K_2PbO_2 + K_2SO_4 + 2H_2O$$

$PbSO_4$ also dissolves on heating in concentrated (30%) CH_3COONH_4 solution probably owing to the formation of $(CH_3COO)Pb^+$ ions, which are dissociated relatively slightly because of the presence of CH_3COO^- ions in the solution.

The acids HCl and HNO_3 also raise the solubility of $PbSO_4$ considerably. This is because the SO_4^{--} ions (yielded by the lead sulphate into the solution) combine with H^+ ions to form HSO_4^- anions, the dissociation of which is suppressed owing to the presence of excess hydrogen ions:

$$\begin{array}{l} PbSO_4 \rightleftarrows Pb^{++} + SO_4^{--} \\ \qquad\qquad\quad + \\ HNO_3 \longrightarrow NO_3^- + H^+ \\ \qquad\qquad\quad \downarrow\uparrow \\ \qquad\qquad\quad HSO_4^- \end{array}$$

The molecular form of the equation for this reaction is*

$$2PbSO_4 + 2HNO_3 = Pb_2(HSO_4)_2 + Pb(NO_3)_2$$

It follows that the above-named acids must be removed from the solution for complete separation of Pb^{++} in the form of $PbSO_4$.

3. Potassium chromate, K_2CrO_4, and dichromate, $K_2Cr_2O_7$, form the extremely insoluble yellow lead chromate ($SP = 1.77 \times 10^{-14}$):

$$Pb^{++} + CrO_4^{--} = \downarrow PbCrO_4$$

$$2Pb^{++} + Cr_2O_7^{--} + H_2O = \downarrow 2PbCrO_4 + 2H^+$$

---

* Acids do not cause any appreciable dissolution of $BaSO_4$, because its solubility product is much smaller than that of $PbSO_4$.

The precipitate dissolves readily in caustic alkalies and with difficulty in dilute nitric acid. It is almost insoluble in ammonia and in acetic acid. This is one of the most important reactions of the Pb^{++} ion.

4. Potassium iodide, KI, precipitates yellow PbI_2 with Pb^{++}:

$$Pb^{++} + 2I^- = \downarrow PbI_2$$

After the precipitate has been formed, add a little water and 2 *N* CH_3COOH solution and heat the test tube; the precipitate dissolves. Immerse the test tube in cold water; PbI_2 is reprecipitated on cooling in the form of shining golden-yellow crystals. This reaction, characteristic for Pb^{++}, is one of the prettiest analytical reactions.

5. Disodium hydrogen phosphate, Na_2HPO_4, precipitates white $Pb_3(PO_4)_2$, which dissolves with some difficulty in dilute nitric and in acetic acid; this fact is sometimes used for separating PO_4^{---} from cations of Groups III, II and I. The equation is

$$3Pb^{++} + 4HPO_4^{--} = \downarrow Pb_3(PO_4)_2 + 2H_2PO_4^-$$

The precipitate is soluble in alkalies and in 2 *N* HNO_3 solution.

6. Benzidine Spot Test. Moisten a piece of filter paper with an ammoniacal solution of 3% H_2O_2 and put a drop of the solution to be tested for Pb^{++} on the moist spot. Hold the paper in the vapour above boiling water. Lead hydroxide (formed by the reaction of the lead salt with NH_4OH) is oxidized by hydrogen peroxide to give brown lead dioxide:

$$Pb(OH)_2 + H_2O_2 = PbO_2 + 2H_2O$$

and excess H_2O_2 is decomposed at the same time.

If the moist spot on the paper is now treated with a drop of benzidine acetate solution, the reagent is oxidized by the PbO_2 which has been formed and the spot turns blue*. The test detects 1.5 μg of Pb^{++}. The dilution limit is 1 : 33,000.

7. Microcrystalloscopic Test. Mix a drop of the solution to be tested for Pb^{++} on a glass slide with a drop of 1% copper acetate solution and evaporate to dryness. Cool and moisten the dry residue with a drop of a concentrated solution of CH_3COONH_4 and KNO_2 in 50% acetic acid. Black cubic crystals of $K_2Pb[Cu(NO_2)_6]$ are formed (see Fig. 6). This is the most characteristic microcrystalloscopic reaction of the Pb^{++} ion. The detectable minimum is 0.03 μg Pb^{++}; the dilution limit is 1 : 33,000.

---

* The equation for the reaction is analogous to that given on p. 283.

69. Reactions of Mercury Cations

Mercury forms two series of salts, mercuric and mercurous. Solutions of the former contain bivalent Hg^{++} cations, and of the latter, Hg_2^{++} cations, in which mercury is electrochemically univalent (since there are two positive charges and two Hg atoms in the ion).

However, if we take into account that when mercurous salts are formed the mercury atoms can combine with each other as well as with acid radicals, we conclude that in reality mercury is bivalent in this case too. This is illustrated by the following structural formulas:

$$\begin{array}{lll} Hg-Cl & Hg-NO_3 & Hg \\ | & | & | \\ Hg-Cl & Hg-NO_3 & Hg \end{array} \diagdown\!\diagup CrO_4, \text{ etc.}$$

Mercury salts are *poisonous*. Mercury ions are colourless in aqueous solutions.

Reactions of the Hg_2^{++} *cation*

1. **Alkalies, NaOH and KOH,** precipitate black mercurous oxide:

$$Hg_2(NO_3)_2 + 2NaOH = \downarrow Hg_2O + H_2O + 2NaNO_3$$

The action of ammonia, a most important qualitative test for Hg_2^{++}, was described in Sec. 66.

2. **Potassium iodide, KI,** forms a greenish precipitate of Hg_2I_2:

$$Hg_2^{++} + 2I^- = \downarrow Hg_2I_2$$

3. **Potassium chromate, K_2CrO_4,** forms a red precipitate of Hg_2CrO_4, insoluble in alkalies and in dilute nitric acid:

$$Hg_2^{++} + CrO_4^{--} = \downarrow Hg_2CrO_4$$

4. **Reduction of Hg_2^{++} to Metallic Mercury.** (a) When excess $SnCl_2$ solution is added to a solution of a mercurous salt, a white precipitate of Hg_2Cl_2 is formed; this turns grey owing to reduction to metallic mercury:

$$Hg_2(NO_3)_2 + SnCl_2 = \downarrow Hg_2Cl_2 + Sn(NO_3)_2$$

$$Hg_2Cl_2 + SnCl_2 = \downarrow 2Hg + SnCl_4$$

(b) When a drop of $Hg_2(NO_3)_2$ solution is put on a bright copper plate (or coin) and left for a while, a grey spot of metallic mercury is formed on the copper:

$$Hg_2(NO_3)_2 + Cu = Cu(NO_3)_2 + \downarrow 2Hg$$

If the solution is washed off with water and the spot is rubbed with a rag or filter paper, it becomes bright.

Reactions of the Hg^{++} *cation*

1. Caustic alkalies, NaOH and KOH, form a yellow precipitate of HgO with mercuric salts, as mercuric hydroxide is unstable (compare Ag^+):

$$Hg^{++} + 2OH^- = Hg(OH)_2$$

$$Hg(OH)_2 = \downarrow HgO + H_2O$$

2. Ammonium hydroxide, NH_4OH, gives white precipitates of ammonobasic compounds, e.g.,

$$HgCl_2 + 2NH_4OH = \downarrow [NH_2Hg]Cl + NH_4Cl + 2H_2O$$

The precipitates are soluble in acids.

3. Potassium iodide, KI, forms an orange-red precipitate of HgI_2 with Hg^{++}:

$$Hg^{++} + 2KI = \downarrow HgI_2 + 2K^+$$

The precipitate dissolves in excess reagent owing to the formation of the very stable complex ion $[HgI_4]^{--}$ ($K_{inst} = 5 \times 10^{-31}$):

$$HgI_2 + 2KI = K_2[HgI_4]$$

If a drop of NH_4OH solution, or of an ammonium salt together with concentrated alkali solution, is added to the resultant solution, a characteristic red-brown precipitate of oxymercuriammonium iodide is formed, e.g.,

$$NH_4Cl + 2K_2[HgI_4] + 4KOH = \downarrow \left[\begin{matrix} & Hg & \\ O & & NH_2 \\ & Hg & \end{matrix} \right] I + KCl + 7KI + 3H_2O$$

We have already used this reaction, under the name of the Nessler reaction, for detection of NH_4^+. It can equally well be used for detection of the Hg^{++} ion.

4. Potassium chromate, K_2CrO_4, forms a yellow precipitate of $HgCrO_4$ which reddens on standing (probably owing to the formation of a basic salt).

5. Reduction of Hg^{++} to Hg_2^{++} and the Metal. (a) The action of $SnCl_2$ on solutions of mercuric salts first gives a white precipitate of Hg_2Cl_2, which is gradually turned grey by excess of stannous chloride as the result of reduction to metallic mercury. The reaction can be represented by the equations

$$2HgCl_2 + SnCl_2 = \downarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

(b) Metallic copper has the same effect on Hg^{++} as on Hg_2^{++}:

$$Hg^{++} + Cu = \downarrow Hg + Cu^{++}$$

Many other metals to the left of mercury in the potential series (p. 327) act similarly.

6. Diphenylcarbazide* forms violet or blue precipitates of unknown composition with mercuric salts. The sensitivity of this reaction diminishes with increasing acidity.

Other heavy metal cations (Cu^{++}, Fe^{+++}, Co^{++}, etc.) form coloured compounds with diphenylcarbazide in neutral or acetic acid solutions, but the reaction is specific for Hg^{++} (provided that chromates and molybdates are absent) in solutions containing 0.2 mole HNO_3 per litre. The detectable minimum (in the presence of nitric acid) is 1 μg Hg^{++}.

Mercury is more difficult to detect in the presence of chlorides owing to the formation of the slightly dissociated salt $HgCl_2$.

7. Microcrystalloscopic Test. Evaporate a drop of a mercuric salt solution *cautiously* almost to dryness with nitric acid. Dissolve 1 part (by weight) of $Co(NO_3)_2$ and 2.5 parts of NH_4CNS in the minimum amount of water, and add a small drop of this reagent to the residue from the evaporation. Blue crystals of $Co[Hg(CNS)_4]$ are formed (see Fig. 33). The detectable minimum is 0.04 μg Hg^{++}. The dilution limit is 1 : 25,000.

70. Reactions of the Cu^{++} Cation

Solutions of cupric salts are blue or green.

1. Caustic alkalies, NaOH and KOH, form a light blue precipitate of $Cu(OH)_2$ with the Cu^{++} ion, turning black on heating owing to formation of CuO:

$$Cu^{++} + 2OH^- = \downarrow Cu(OH)_2$$

$$Cu(OH)_2 = CuO + H_2O$$

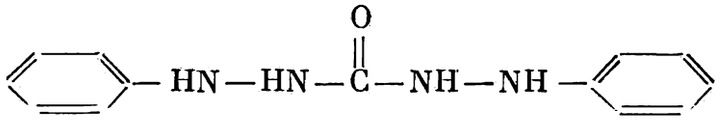
Cupric hydroxide is weakly amphoteric and is therefore partially soluble in excess KOH or NaOH (especially on heating) to form cuprites.

The Cu^{++} ion forms blue complex compounds, not precipitated by alkalies, in the presence of glycerol, tartaric and citric acids, and certain other organic compounds containing hydroxyl groups. Confirm this by experiment, by adding glycerol or tartaric acid followed by caustic alkali to a solution of a cupric salt.

2. Ammonium hydroxide, NH_4OH, added in small amounts, precipitates greenish basic salts, such as $(CuOH)_2SO_4$, readily soluble

---

* The formula is



in excess reagent. The solution contains a complex copper ammine of an intense blue colour.

This very characteristic reaction of the Cu^{++} ion may be represented by the following ionic equations:

$$2Cu^{++} + SO_4^{--} + 2NH_4OH = \downarrow (CuOH)_2SO_4 + 2NH_4^+$$

$$(CuOH)_2SO_4 + 8NH_4OH = 2[Cu(NH_3)_4]^{++} + SO_4^{--} + 2OH^- + 8H_2O$$

When acidified, the ammine complex is decomposed; the NH_3 molecules combine with H^+ ions to form a more stable NH_4^+ complex (compare the analogous reaction with Ag^+). The deep blue colour of the solution changes to pale blue (colour of the Cu^{++} ion). The $[Cu(NH_3)_4]^{++}$ complex is also decomposed by the action of H_2S, as the Cu^{++} ion concentration in solution is sufficient to exceed the solubility product of CuS, which is precipitated.

3. Potassium ferrocyanide, $K_4[Fe(CN)_6]$, gives a red-brown precipitate of copper ferrocyanide with the Cu^{++} ion:

$$2Cu^{++} + [Fe(CN)_6]^{==} = \downarrow Cu_2[Fe(CN)_6]$$

The precipitate is insoluble in dilute acids but dissolves in ammonia (to form a complex compound). It is also decomposed by alkalies:

$$Cu_2[Fe(CN)_6] + 4OH^- = \downarrow 2Cu(OH)_2 + [Fe(CN)_6]^{==}$$

This reaction is more sensitive than the reaction with NH_4OH.

4. Sodium thiosulphate, $Na_2S_2O_3$, decolourizes an acidified solution of a copper salt owing to the formation of a complex salt. If the solution is heated, a dark brown mixture of Cu_2S and sulphur is precipitated. The reaction may be represented by the equation

$$2Cu^{++} + 2S_2O_3^{--} + 2H_2O = \downarrow Cu_2S + \downarrow S + 4H^+ + 2SO_4^{--}$$

As the Cd^{++} ion does not form a sulphide precipitate with $Na_2S_2O_3$ in acid solution, this reaction can be used for separating Cu^{++} from Cd^{++}.

5. Metallic aluminium, iron and zinc reduce the Cu^{++} ion to the metal, which appears in the form of a red spongy mass, e.g.,

$$3Cu^{++} + 2Al = \downarrow 3Cu + 2Al^{+++}$$

This reaction can also be used to separate Cu^{++} from Cd^{++}.

The positions of the copper and cadmium in the potential series (p.327) suggest that both metals should be displaced by aluminium, iron, and zinc from solutions of their salts. However, if this reaction is carried out in the presence of H_2SO_4 metallic cadmium is not formed, because it is soluble in acids. On the other hand, in accordance

with its position to the right of hydrogen in the potential series, metallic copper does not dissolve in dilute H_2SO_4 and is therefore liberated in its presence.

Copper is not precipitated in the presence of HNO_3, which dissolves it readily:

$$3Cu + 2NO_3^- + 8H^+ = 3Cu^{++} + 2NO\uparrow + 4H_2O$$

Therefore HNO_3 must be removed completely before separation of Cu^{++} from Cd^{++}; this is achieved by evaporation* of the solution with H_2SO_4.

6. Benzidine in the Presence of Potassium Cyanide, KCN. Cupric cyanide, $Cu(CN)_2$, is extremely unstable and is reduced to CuCN with liberation of cyanogen, $(CN)_2$, as soon as it is formed. Therefore cupric cyanide can oxidize benzidine to form a blue compound; this is the basis of the spot test described below.

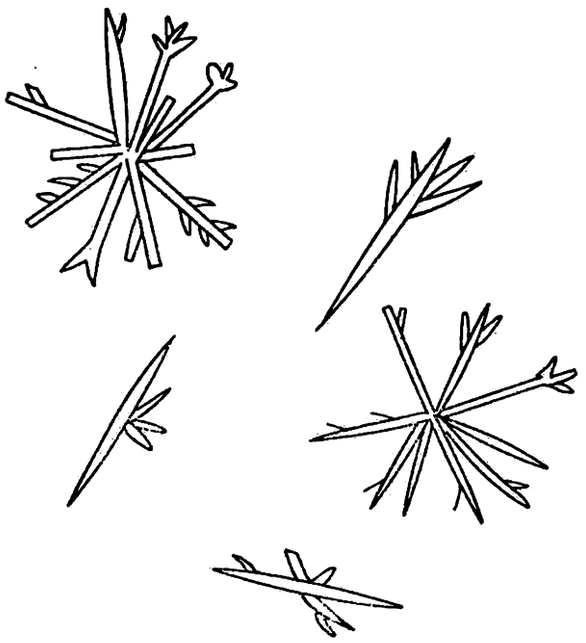


Fig. 37. Crystals of $Cu[Hg(CNS)_4]$

Put a drop of the unknown solution, a drop of benzidine solution, and a drop of KCN solution**, *in that order*, on a strip of filter paper. The spot turns blue in the presence of Cu^{++}. No Ag^+ or Fe^{++} ions must be present.

7. Zinc Acetate, $(CH_3COO)_2 \cdot Zn$, and Ammonium Tetrathiocyanatomercurate, $(NH_4)_2[Hg(CNS)_4]$. Add 1 drop each of 1% $(CH_3COO)_2Zn$ and $(NH_4)_2[Hg(CNS)_4]$ solutions to a drop of the acidified unknown solution on a spot plate. A violet precipitate of a complex compound of zinc, mercury and copper thiocyanates is formed. The copper salt solution must be *extremely dilute* for the test to work; otherwise yellow-green $Cu[Hg(CNS)_4]$ is precipitated. No Fe^{+++}, Co^{++} or Ni^{++} must be present. The test detects 0.1 μg of Cu^{++}. The dilution limit is 1 : 500,000.

8. Microcrystalloscopic Test. Add a drop of $(NH_4)_2[Hg(CNS)_4]$ solution to a drop of the unknown solution slightly acidified with

---

* The above also applies to separation of Cu^{++} by means of $Na_2S_2O_3$, which is oxidized by nitric acid to give Na_2SO_4 and sulphur.

** Instead of KCN, a solution of KBr (unsaturated) or NH_4CNS may be used, because $CuBr_2$ and $Cu(CNS)_2$ are as unstable as $Cu(CN)_2$.

CH_3COOH. Characteristic yellow-green crystals of $Cu[Hg(CNS)_4]$ are precipitated (Fig. 37). The test detects 0.1 μg of Cu^{++}. The dilution limit is 1 : 10,000. The Cd^{++} ion also gives a crystalline precipitate with $(NH_4)_2$ $[Hg(CNS)_4]$.

9. **Dry-Way Tests.** *a. Flame colouration.* Copper salts give a blue or green flame.

b. Grinding of solid copper salts with solid NH_4CNS results in immediate blackening of the mixture owing to formation of cupric thiocyanate*:

$$CuSO_4 + 2NH_4CNS = Cu(CNS)_2 + (NH_4)_2SO_4$$

71. Reactions of the Cd^{++} Cation

The Cd^{++} ion is colourless in aqueous solutions.

1. **Caustic alkalies, NaOH and KOH,** precipitate white cadmium hydroxide, $Cd(OH)_2$, soluble in acids.

2. **Ammonium hydroxide, NH_4OH,** precipitates $Cd(OH)_2$, which dissolves in excess owing to the formation of a complex ammine:

$$Cd^{++} + 2OH^- = \downarrow Cd(OH)_2$$

$$Cd(OH)_2 + 4NH_4OH = [Cd(NH_3)_4]^{++} + 2OH^- + 4H_2O$$

In contrast to $[Cu(NH_3)_4]^{++}$, the $[Cd(NH_3)_4]^{++}$ complex is colourless. The formation of these complexes is utilized in analysis for separating Cu^{++} and Cd^{++} ions from Bi^{+++}, as the latter forms a basic salt with ammonia, insoluble in excess.

3. **Hydrogen sulphide, H_2S,** in neutral, alkaline, and not excessively acid solutions (at $pH \geqslant 0.5$) gives a yellow precipitate of CdS, which is insoluble in caustic alkalies and in sodium sulphide (distinction from arsenic sulphides). Excess of acids or of chlorides interferes with this most characteristic reaction of the Cd^{++} ion. In contrast to CdS, cupric sulphide CuS, which has a much smaller solubility product, is formed in strongly acidic solutions even in the presence of a large excess of NH_4Cl. This fact can be used for separating Cu^{++} from Cd^{++}, which occur together in the course of analysis in the form of complex ammines. Various methods can be used for the separation.

(a) The ammoniacal solution containing $[Cu(NH_3)_4]^{++}$ and $[Cd(NH_3)_4]^{++}$ ions is slightly acidified with 2*N* HCl solution until the dark blue colour of the copper complex has changed to the pale blue

---

* The same reaction takes place when solutions of cupric salts and thiocyanates are mixed, but in this case the original black $Cu(CNS)_2$ precipitate gradually turns white on standing (more rapidly in the presence of H_2SO_3) owing to reduction to CuCNS with liberation of thiocyanogen $(CNS)_2$:

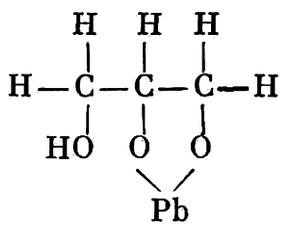
$$2Cu(CNS)_2 = 2CuCNS + (CNS)_2$$

colour of the Cu^{++} ion, followed by an equal volume of 2 *N* HCl solution (or 1 ml of concentrated HCl to each 10-11 ml of the solution). The resultant solution (1 *N* with respect to HCl) is heated nearly to boiling and saturated with hydrogen sulphide while still hot. After complete precipitation has been confirmed, the CuS precipitate is filtered off and rejected. The filtrate is *diluted with 3-4 times its own volume of water** and H_2S is passed again. A yellow precipitate of CdS indicate sthe presence of Cd^{++}.

(b) 2 *N* HCl is added to the ammoniacal solution until acid, followed by solid NH_4Cl; the solution is saturated with NH_4Cl by shaking. It is then heated and H_2S is passed. When CuS has been completely precipitated, it is filtered off and rejected. The filtrate is diluted with several times its own volume of water and H_2S is passed again. A yellow precipitate of CdS indicates the presence of Cd^{++}.

(c) The ammoniacal solution is slightly acidified until the intense blue colour of the copper ammine complex has changed to the light blue of the Cu^{++} ion. It is then heated and H_2S is passed until the sulphides of copper and cadmium have been completely precipitated. The precipitate is filtered off and warmed with a mixture of 2 *N* HCl and water. This dissolves CdS while CuS remains in the residue. The precipitate is filtered off, the filtrate is *diluted with thrice its own volume of water* and H_2S is passed through it or *freshly prepared* H_2S water is added.

4. Glycerol, $CH_2OH—CHOH—CH_2OH$, does not form complexes with Cd^{++} ions. This distinguishes Cd^{++} from Pb^{++}, Cu^{++}, and Bi^{+++}, which form soluble glycerates, such as



from solutions of which Pb^{++} is not precipitated by alkalies. Therefore if an excess of alkali is added on heating to a solution containing all these cations in the presence of glycerol, Cd^{++} is completely precipitated as $Cd(OH)_2$ while Pb^{++}, Cu^{++}, and Bi^{+++} remain in solution in the form of glycerates. This greatly simplifies the analysis of the second subgroup of Group IV, because Pb^{++}, Cu^{++} and Bi^{+++} can be detected in the filtrate by the fractional method after separation of Cd^{++}.

* Unless the solution is diluted CdS is not precipitated. This is not only because the S^{--} ion concentration is lowered by the increased, H^+ ion concentration, but also because the Cd^{++} concentration is lowered owing to formation of the $[CdCl_4]^{--}$ complex. Therefore CdS is not precipitated even from a moderately acid solution if solid NH_4Cl is first added in excess.

The Cu^{++} ion is detected by the blue colour of the solution due to copper glycerate, and also by the reaction with $K_4[Fe(CN)_6]$ in a portion of the solution acidified with acetic acid. The Pb^{++} ion can be detected by the action of K_2CrO_4 on the solution acidified with CH_3COOH*. Finally, Bi^{+++} is detected by reduction to metallic bismuth by the action of stannite solution (see Sec. 72, 4). The alkaline solution to be tested for bismuth, obtained after separation of $Cd(OH)_2$, is added drop by drop to Na_2SnO_2 solution. Blackening of the contents of the test tube indicates the presence of Bi^{+++}.

As a confirmatory test, the $Cd(OH)_2$ precipitate formed by the action of alkali in the presence of glycerol is filtered off, washed, dissolved in dilute HCl and reprecipitated by alkali in the presence of glycerol (to remove the small amounts of copper and bismuth hydroxides coprecipitated during the first precipitation). The $Cd(OH)_2$ precipitate is filtered off, dissolved in 2 *N* HCl, and diluted with four volumes of water; H_2S is passed through the diluted solution. A yellow precipitate of CdS confirms the presence of Cd^{++}.

5. **Potassium cyanide, KCN,** forms a white amorphous precipitate of $Cd(CN)_2$ with Cd^{++} ions; this dissolves readily in excess reagent to form the complex ion $[Cd(CN)_4]^{--}$:

$$Cd^{++} + 2CN^- = \downarrow Cd(CN)_2$$

$$Cd(CN)_2 + 2CN^- = [Cd(CN)_4]^{--}$$

The cadmium cyanide complex partially dissociates into its constituent ions, CN^- and Cd^{++} ($K_{inst} = 1.4 \times 10^{-17}$). The Cd^{++} ion concentration in solution is then sufficient to exceed the solubility product of CdS when H_2S is passed, so that the sulphide is precipitated.

The Cu^{++} ion first forms a yellow precipitate of $Cu(CN)_2$ with the CN^- ion; however, this is unstable and is immediately reduced to white cuprous cyanide CuCN. The latter dissolves in excess cyanide to form the complex $[Cu(CN)_4]^{---}$:

$$Cu^{++} + 2CN^- = \downarrow Cu(CN)_2$$

$$2Cu(CN)_2 = 2CuCN + (CN)_2$$

$$CuCN + 3CN^- = [Cu(CN)_4]^{---}$$

In contrast to the cadmium cyanide complex, the copper complex is very stable ($K_{inst} = 5 \times 10^{-28}$) and is not decomposed by H_2S. This makes it possible to detect Cd^{++} during analysis without separation of Cu^{++}. A solution of KCN is added to a mixture of the copper and cadmium ammine complexes until the blue colour of the $[Cu(NH_3)_4]^{++}$ ion disappears, followed by 2-3 more drops in excess. The $[Cu(NH_3)_4]^{++}$ complex is converted into the more stable $[Cu(CN)_4]^{---}$ complex. If H_2S is passed through the solution after addition of KCN, yellow CdS is precipitated in the presence of Cd^{++}.

---

* If too little CH_3COOH is added, yellow bismuthyl chromate may be precipitated. Unlike $PbCrO_4$, it is insoluble in alkalies but dissolves in CH_3COOH.

It must be remembered when carrying out this test that KCN *is intensely poisonous* and must be handled with great care. *Never add* KCN *to acid solutions, as the volatile and highly poisonous hydrocyanic acid,* HCN, *would be formed. After experiments with cyanides the solutions should be poured away down the sink or in a flask in a fume cupboard.*

6. **Microcrystalloscopic Test.** Add a drop of $(NH_4)_2[Hg(CNS)_4]$ solution to a drop of a neutral or weakly acidic solution of a cadmium salt. Colourless crystals of $Cd[Hg(CNS)_4]$ are precipitated

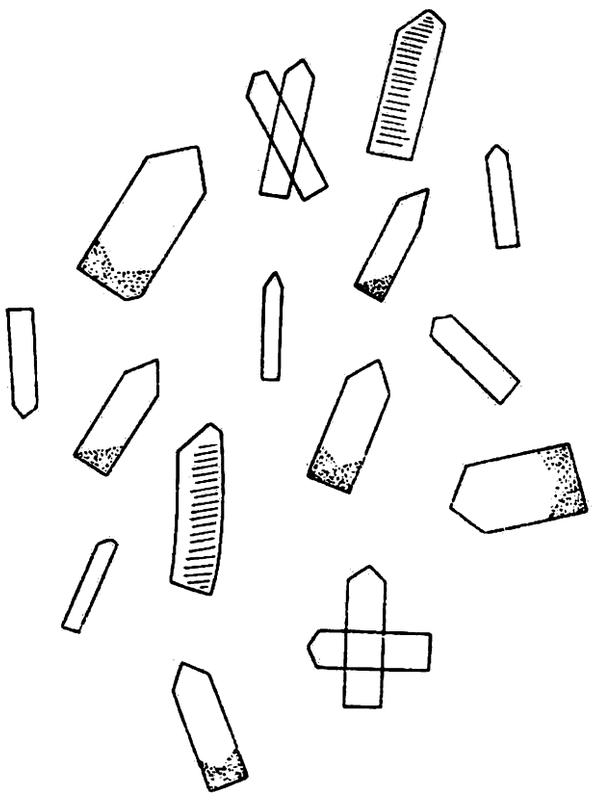


Fig. 38. Crystals of $Cd[Hg(CNS)_4]$

(Fig. 38). The detectable minimum is 1 μg Cd^{++}, and the dilution limit is 1 : 1,000. In the presence of copper, cobalt, ferric iron and zinc salts the crystals are different in colour and shape owing to the formation of mixed crystals.

72. Reactions of the Bi^{+++} Cation

In aqueous solutions the Bi^{+++} ion is colourless.

1. **Action of Water (Hydrolysis).** Dilute $BiCl_3$ solution with a large volume of water. A white basic salt is precipitated; its composition corresponds to the formula BiOCl. The course of the reaction may be represented as follows.

First, a basic salt containing two hydroxyl groups in the molecule is formed as the result of hydrolysis:

$$BiCl_3 + 2H_2O = Bi(OH)_2Cl + 2HCl$$

However, this salt is unstable and immediately splits off water to give a new basic salt, BiOCl, with one bivalent atom (oxygen) in place of two hydroxyl groups:

$$Bi(OH)_2Cl = BiOCl + H_2O$$

Thus, because of the liberation of water a molecule of a basic salt may not contain any hydroxyl groups.

Bismuth nitrate, $Bi(NO_3)_3$, also undergoes hydrolysis to form the basic salt $BiONO_3$. However, the reaction does not go so well with bismuth nitrate, as $BiONO_3$ is more soluble than BiOCl; it is therefore advisable to add a chloride, such as NaCl, to the $Bi(NO_3)_3$ solution; BiOCl is then precipitated in its presence.

The univalent group —Bi=O in basic bismuth salts is known as the *bismuthyl* group. Therefore BiOCl and $BiONO_3$ can be called bismuthyl chloride and nitrate respectively.

The formation of a basic salt is a reversible reaction. Therefore when hydrochloric acid is added to BiOCl and the liquid is heated, the precipitate dissolves:

$$BiOCl + 2HCl = BiCl_3 + H_2O$$

The basic salt is reprecipitated when the solution is diluted with water.

2. Caustic alkalies, NaOH and KOH, give a white precipitate of bismuth hydroxide, soluble in acids but insoluble in alkalies:

$$Bi^{+++} + 3OH^- = \downarrow Bi(OH)_3$$

3. Ammonium hydroxide, NH_4OH, precipitates white basic salts of variable composition, dependent on the concentration and temperature.

4. Potassium and sodium stannites, K_2SnO_2 and Na_2SnO_2, reduce Bi^{+++} to form a black precipitate of metallic bismuth. To carry out the test, add (in the cold) an excess of 2 *N* alkali solution to $SnCl_2$ solution, so that the initially precipitated $Sn(OH)_2$ dissolves to form a stannite:

$$SnCl_2 + 2NaOH = 2NaCl + \downarrow Sn(OH)_2 \text{ (or } H_2SnO_2)$$

$$H_2SnO_2 + 2NaOH = Na_2SnO_2 + 2H_2O$$

Add a solution of a bismuth salt to this stannite solution. Black metallic bismuth is precipitated:

$$Bi(NO_3)_3 + 3NaOH = Bi(OH)_3 + 3NaNO_3$$

$$2Bi(OH)_3 + 3Na_2SnO_2 = \downarrow 2Bi + 3Na_2SnO_3 + 3H_2O$$

The compound Na_2SnO_3 formed in this reaction is called sodium stannite. It is a salt of metastannic acid, H_2SnO_3, corresponding to the oxide SnO_2.

The ionic form of the equation is

$$2Bi(OH)_3 + 3SnO_2^{--} = \downarrow 2Bi + 3SnO_3^{--} + 3H_2O$$

Another way of carrying out this most important reaction of the Bi^{+++} ion is to treat with stannite solution the precipitate of basic bismuth salts obtained in the separation of Bi^{+++} from Cu^{++} and Cd^{++} by the action of excess NH_4OH.

The reaction also works with an alkaline solution of the bismuth glycerol complex, as a sufficient concentration of Bi^{+++} ions is formed by dissociation of this compound.

Addition of concentrated alkali and heating should be avoided in this reaction, otherwise a black precipitate of metallic tin may form owing to decomposition of the stannite:

$$2Na_2SnO_2 + H_2O = Na_2SnO_3 + \downarrow Sn + 2NaOH$$

If the excess of alkali is insufficient, black stannous oxide SnO may be precipitated on standing.

5. **Potassium dichromate, $K_2Cr_2O_7$,** forms a yellow precipitate of bismuthyl dichromate with bismuth salts:

$$2Bi^{+++} + Cr_2O_7^{--} + 2H_2O = \downarrow (BiO)_2Cr_2O_7 + 4H^+$$

The precipitate resembles lead chromate in appearance, but differs from the latter by being soluble in acetic acid and insoluble in alkalies.

6. **Disodium hydrogen phosphate, Na_2HPO_4,** gives a white powdery precipitate of bismuth phosphate with the Bi^{+++} ion:

$$Bi^{+++} + 2HPO_4^{--} = \downarrow BiPO_4 + H_2PO_4^-$$

The precipitate is almost insoluble in dilute nitric acid. Because of this, the formation of bismuth phosphate may be used for separating PO_4^{---} ions (which interfere in the separation of Groups III and II by the action of ammonium sulphide) in systematic analysis of the cations (see p. 501).

7. **Potassium iodide, KI,** added to fairly concentrated acidified solutions of bismuth salts, gives a black precipitate of BiI_3, soluble in excess KI to form complex $[BiI_4]^-$ ions, orange in colour:

$$Bi^{+++} + 3I^- = \downarrow BiI_3$$

$$BiI_3 + I^- = [BiI_4]^-$$

If the solution is moderately diluted with water, black BiI_3 is reprecipitated:

$$[BiI_4]^- = \downarrow BiI_3 + I^-$$

Greater dilution gives an orange precipitate of the basic salt instead of BiI_3:

$$[BiI_4]^- + H_2O = \downarrow BiOI + 3I^- + 2H^+$$

8. Thiourea, $SC(NH_2)_2$. A yellow colour appears when a solution of thiourea in nitric acid acts on a solution of a bismuth salt, owing

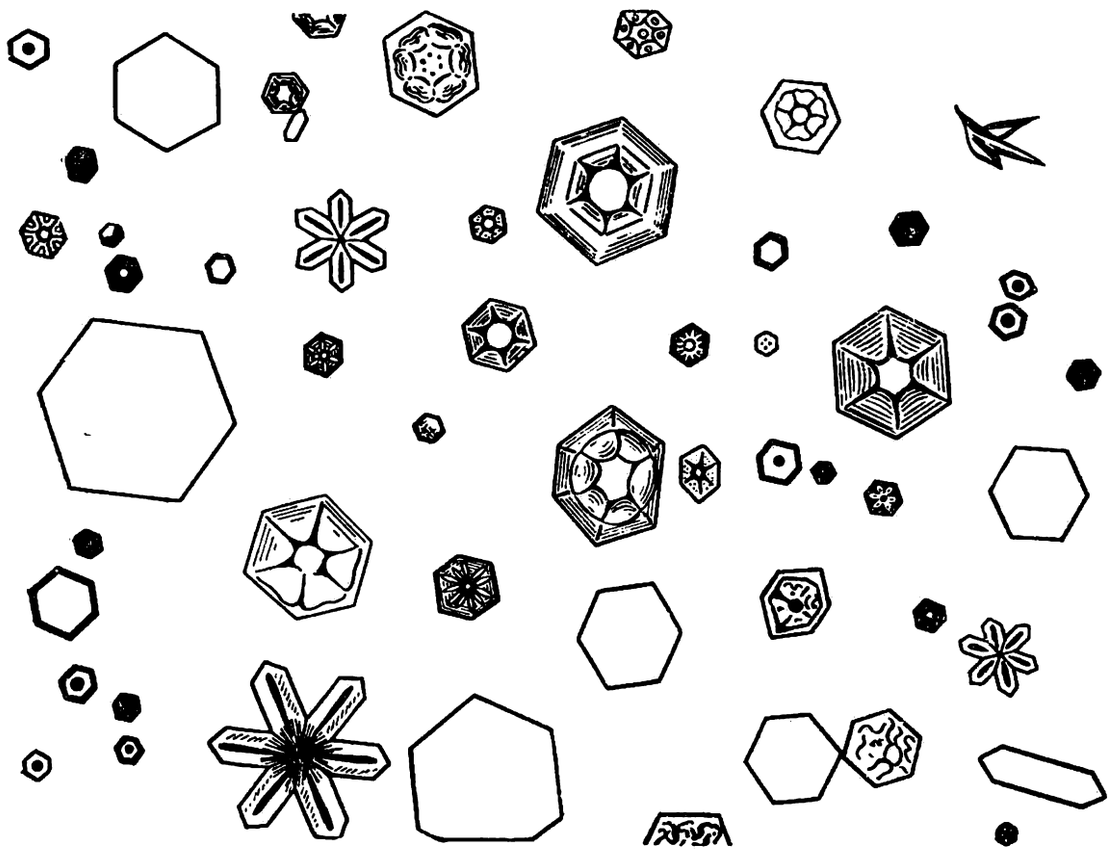


Fig. 39. Crystals of $Rb_2[BiI_5]\cdot 2.5H_2O$

to the formation of complex $[SC(NH_2)_2]_3Bi^{+++}$ ions. Thiourea forms insoluble compounds with Pb^{++} and Cd^{++} ions, but these do not interfere with the detection of Bi^{+++}.

9. Hydroxyquinoline, C_9H_7ON, and potassium iodide, KI, give an orange-red precipitate with solutions of bismuth salts (a compound of hydroxyquinoline with the complex acid $HBiI_4$, having the formula $C_9H_7ON\cdot HBiI_4$). The solution must be free from the cations Ag^+, Hg_2^{++} and Pb^{++}, which precipitate I^-, and from oxidizing agents (in particular, Cu^{++} and Fe^{+++}) which oxidize I^- to I_2. The interfering effect of the latter can be prevented if the reaction is carried out in the presence of $Na_2S_2O_3$ or $SnCl_2$. Proceed as follows. Add two or three drops of the reagent (mixture of hydroxyquinoline and KI) and one drop of starch solution to several drops of the solution to be tested. If the solution becomes blue (owing to liberation of iodine by

oxidizing agents present) add $Na_2S_2O_3$ solution drop by drop until the colour disappears. An orange-red precipitate is formed in the presence of Bi^{+++}.

The reaction can also be conducted as a spot test. Moisten a strip of filter paper with $SnCl_2$ solution and then apply a drop of the unknown solution and a drop of the reagent. To confirm complete reduction of oxidizing agents, moisten the spot with a drop of starch solution. An orange-red colour indicates the presence of Bi^{+++}.

10. Microcrystalloscopic Test. Add a grain of KI and of RbCl (or CsCl) to a drop of a solution of a bismuth salt in hydrochloric acid*. Red hexagonal crystals of a complex salt, having the composition $Rb_2[BiI_5]\cdot 2.5H_2O$ or $Cs_2[BiI_5]\cdot 2.5H_2O$ (Fig. 39) are formed**. The Sb^{+++} ion gives similar crystals. Large amounts of Sn^{++++} or Pb^{++} ions interfere.

73. Analysis of Mixtures of Group IV Cations

The effects of the most important reagents for Group IV cations are compared in Table 22.

The analytical scheme for mixtures of cations of Groups IV-I, based on these reactions, is given in Table 23 (pp. 374-375).

As before, the unknown solution may contain a precipitate insoluble in dilute HCl. This precipitate may contain the chlorides of silver, lead, and univalent mercury, and the sulphates of lead and of Group II cations. Methods for analyzing all other substances which are insoluble in acids will be discussed later (Sec. 112).

ANALYTICAL PROCEDURE FOR MIXTURES OF CATIONS OF GROUPS IV-I

1. Preliminary Inferences and Tests. As always, the analysis is started with preliminary observations (inferences) and tests. First note the colour of the solution, which may sometimes indicate the presence of Cu^{++}. To intensify the colour, it is helpful to add 1-2 ml of 13 *N* ammonia solution to 1 ml of the unknown solution in order to convert Cu^{++} into $[Cu(NH_3)_4]^{++}$. It must be remembered, however, that a weaker blue colour may appear owing to formation of a nickel ammine, $[Ni(NH_3)_6]^{++}$.

Separate portions of the solution must be tested for Fe^{+++} and Fe^{++} ions (because after treatment with H_2S all the iron in solution will be in the form of Fe^{++} and its original valency cannot then be established), and for NH_4^+, as this ion is subsequently introduced when

---

* A large excess of HCl must not be present.

** The $Cs_2[BiI_2]\cdot 2.5H_2O$ crystals are smaller than $Rb_2[BiI_5]\cdot 2.5H_2O$, but are of the same shape.

the acidity of the solution is adjusted before precipitation of the Group IV cations by means of hydrogen sulphide.

Moreover, the pH of the solution must be determined as usual. A low pH value may be due to the presence of free acids, or of highly hydrolyzed salts of bismuth and mercury* or of iron. If the pH does not alter appreciably after a portion of the solution has been *carefully* neutralized until a permanent turbidity has appeared, this is a preliminary indication of the presence of some of these cations. If the solution is alkaline, this means that of the Group IV cations only PbO_2^{--}, $[Cu(NH_3)_4]^{++}$, $[Cd(NH_3)_4]^{++}$, and certain other complex ions such as complex cyanides, tartrates, glycerates, etc., may be present.

2. Separation of the First Subgroup of Group IV. Add a small amount (1-3 ml) of HCl solution, obtained by dilution of the concentrated acid with an equal volume of water, to the whole solution, regardless of whether it contains a precipitate or not. Test for complete precipitation and if necessary add more HCl (a large excess should be avoided). Warm the liquid with the precipitate (to ensure that the basic salts dissolve in HCl as much as possible) and then cool under the tap so that the lead chloride which dissolved on heating is reprecipitated. Filter off the precipitate through a filter moistened with HCl into a flask rinsed out with HCl (otherwise the filtrate may be turbid owing to precipitation of basic salts). Wash the precipitate with cold distilled water containing a little HCl.

In addition to AgCl, Hg_2Cl_2, $PbCl_2$, the precipitate may contain constituents of the unknown solution which are insoluble or sparingly soluble in HCl, such as $PbSO_4$, Group II sulphates, or basic salts of bismuth (and also of antimony and tin if Group V cations are present**) as they may not have dissolved completely in HCl. Investigate the precipitate according to 3.

The solution, containing all the other cations of Groups IV-I together with the added HCl, is investigated as described in 8.

3. Dissolving $PbCl_2$, Detection of Pb^{++}. Treat the washed precipitate on the filter with about 5 ml of boiling water. This dissolves part of the $PbCl_2$. Test for Pb^{++} in the solution by the reactions with K_2CrO_4 or KI.

If Pb^{++} is present, continue to wash the precipitate with hot water until all $PbCl_2$ has been dissolved out (i.e., to a negative reaction with K_2CrO_4). Investigate the residue according to 4.

---

* According to N. A. Tananaev, solutions of bismuth and mercuric salts (not acidified) have pH $\approx$ 2, with the exception of $HgCl_2$, solutions of which have pH $\approx$ 4.

** We refer here to antimony and tin ions because this description of the analytical procedure will be used with reference to analysis of mixtures containing cations of all five groups.

Reagents	Cations		
	Ag^+	Pb^{++}	Hg_2^{++}
H_2S in acid solution, or $(NH_4)_2S$	Black ppt. Ag_2S	Black ppt. **PbS**	Black ppt. $HgS + Hg$
HCl and chlorides	White ppt. of **AgCl**, soluble in NH_4OH *	White ppt. of **$PbCl_2$**, soluble in hot water	White ppt. of **Hg_2Cl_2**, blackened by NH_4OH **
KOH or NaOH	Brown ppt. Ag_2O	White ppt. of $Pb(OH)_2$ ***, soluble in excess alkali	Black ppt. Hg_2O
NH_4OH in excess	Formation of $[Ag(NH_3)_2]^+$ ions	White ppt. $Pb(OH)_2$	Black ppt. $[NH_2Hg]NO_3 + + Hg$
H_2O	—	—	—
H_2SO_4	—	White ppt. **$PbSO_4$**	White ppt. Hg_2SO_4
$SnCl_2$ or Na_2SnO_2	Black ppt. Ag	—	White ppt., gradually blackens, **$Hg_2Cl_2 \rightarrow \rightarrow$ Hg**

* Formation of complex $[Ag(NH_3)_2]^+$ ions.
** Formation of black mixture of $[NH_2Hg]Cl + Hg$.
*** Not formed in the presence of glycerol.
**** Formed in the presence of glycerol.

Table 22

Group IV Cations

	Cations			
	Hg^{++}	Cu^{++}	Cd^{++}	Bi^{+++}
	Black ppt. of **HgS, insoluble in HNO_3**	Black ppt. **CuS**	Yellow ppt. **CdS**	Black ppt. **Bi_2S_3**
	—	—	—	—
	Yellow ppt. HgO	Blue ppt. of $Cu(OH)_2$ ***	White ppt. of $Cd(OH)_2$ ****	White ppt. of $Bi(OH)_3$ ***
	White ppt. $[NH_2Hg]Cl$	Formation of deep blue **$[Cu(NH_3)_4]^{++}$** ions	Formation of $[Cd(NH_3)_4]^{++}$ ions	White ppt. of **basic salts**
	—	—	—	White ppt. of BiOCl, soluble in excess acid
	—	—	—	—
	White ppt., gradually blackens, **$Hg_2Cl_2 \rightarrow$ $\rightarrow$ Hg**	—	—	Black ppt. **Bi**

4. Separation of Ag^+ and Detection of Hg_2^{++}. After treatment of the precipitate with hot water as described in 3, treat the residue on the filter with a few millilitres of 2 *N* NH_4OH. This dissolves AgCl to give the complex salt $[Ag(NH_3)_2]Cl$, while Hg_2Cl_2 is converted into a mixture of $[HgNH_2]Cl$ + Hg (black in colour) which remains on the filter. Thus, *instantaneous* blackening of the precipitate by the action of NH_4OH indicates* the presence of Hg_2^{++}.

This inference is conclusive only if Group V ions are absent, because the precipitate may also turn black owing to reduction of AgCl to metallic silver by basic stannous salts. This means that if Group V ions may be present the final decision concerning the presence of Hg_2^{++} can be made only after the confirmatory tests for mercury described in 7, (a). Investigate the ammoniacal solution according to 5, and the residue according to 6.

5. Detection of Ag^+. To a portion of the ammoniacal solution add a drop of phenolphthalein indicator followed by HNO_3 until the colour disappears. A white precipitate (or turbidity) of AgCl indicates the presence of silver. If a large amount of Hg_2^{++} is present, a negative result in this test is *unreliable*, because Ag^+ ions may be reduced completely by metallic mercury (formed by the action of ammonia on Hg_2Cl_2) to silver metal. In such cases, if Ag^+ is not found in the solution, test for it in the precipitate, 7, (a).

6. Detection of Pb^{++}. If the nitric acid test in the ammoniacal solution as described in 5 gave a positive result, continue to treat the precipitate on the filter with ammonia until AgCl has been removed completely (i.e., to a negative test for Ag^+). Then wash the precipitate once with water and treat it on the filter with warm 30% CH_3COONH_4 solution, passing the filtrate once or twice through the same filter. This dissolves part of the $PbSO_4$ and Pb^{++} can be detected in the solution by tests with K_2CrO_4 or KI. Wash the residue on the filter and investigate according to 7.

7. Dissolving the Basic Salts. Treat the residue from the ammonium acetate treatment (according to 6) on the filter with 10 ml of hot 2 *N* HCl. This dissolves basic salts of bismuth (and of antimony and tin if Group V ions are present). If it is known that Group V ions are absent, the solution must be tested for Bi^{+++} by its characteristic reactions (action of water, reaction with Na_2SnO_2 in the presence of excess NaOH, etc.; see Sec. 72). Otherwise combine this solution with the filtrate from the separation of the silver subgroup by the action of HCl (as described in 2).

(a) As stated in 5, if the test for Ag^+ in the filtrate is negative in the presence of Hg_2^{++} the precipitate must be tested for silver. After treatment of the

* Slow blackening of the precipitate may be due to conversion of $PbSO_4$ or basic bismuth salts into the respective sulphides by H_2S present in the laboratory air.

residue with HCl according to 7, transfer it to a porcelain basin and warm it with a small amount (1-2 ml) of a mixture of HNO_3 (sp. gr. 1.2) and HCl (sp. gr. 1.19). This dissolves mercury in the form of $HgCl_2$ while silver is converted into AgCl which remains in the precipitate together with Group II sulphates and $PbSO_4$ (if the latter was not dissolved completely when the precipitate was treated with ammonium acetate as described in 6). Dilute the solution with water, filter off and wash the precipitate and treat it with ammonia on the filter. Test for Ag^+ in the ammoniacal solution according to 5.

Test the filtrate for Hg^{++} by adding $SnCl_2$ solution; a white precipitate which turns grey ($Hg_2Cl_2 \rightarrow Hg$) confirms the presence of mercury.

(b) If an insoluble residue remains after treatment of the precipitate with ammonia [see (a), above], test its solubility in warm NaOH. If the precipitate dissolves completely, it contains lead sulphate only. If there is a residue, test it for Group II sulphates as described on p. 172.

8. Adjusting the Acidity of the Solution and Precipitation of Group IV Cations by Hydrogen Sulphide. To ensure complete precipitation of Group IV cations while zinc sulphide is not precipitated, the H^+ ion concentration must be adjusted to a suitable level, about 0.3 *M* (p. 346), which corresponds to pH $\approx$ 0.5. This is done as follows. Add the filtrate from the separation of the first subgroup of Group IV (see 2) to the solution obtained when the basic salts were dissolved as described in 7, and neutralize the acid, the concentration of which is unknown. Add 25% ammonia solution drop by drop until alkaline to litmus. Then add 2 *N* HCl solution, also drop by drop, until the last 1-2 drops make the solution acid again. To this almost neutral solution add one-fifth of its own volume of 2 *N* HCl, which will ensure the required acidity. (If a residue of basic salts which did not dissolve in HCl remains after all these operations, it may be disregarded, because the basic salts will be completely converted into the less soluble sulphides when H_2S is passed.)

Heat the solution almost to boiling, pass a slow stream of H_2S through it for about 10-15 minutes, add an equal volume of cold distilled water, and pass hydrogen sulphide again for 5-10 minutes*. Test for complete precipitation by filtering off 1-2 ml of the liquid and adding an equal volume of *freshly prepared* H_2S water**. If a precipitate is formed, pass H_2S again through the whole solution after diluting it again with water. When the precipitation is complete, filter off the precipitate and wash it with H_2S water (to prevent oxidation of the sulphides by atmospheric oxygen) containing a small amount of NH_4Cl. Investigate the precipitate according to 9.

---

* The significance of various conditions in precipitation by hydrogen sulphide is explained on pp. 346-349.

** Another advantage of using H_2S water is that it avoids error if incomplete precipitation is due to excessive acidity of the solution. However, it must be freshly prepared and must smell strongly of H_2S.

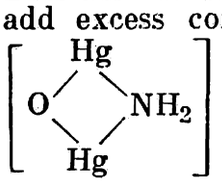
Test the filtrate first for Zn^{++} as follows. To about 1 ml of the filtrate immediately add an equal volume of formate buffer* (p. 285) and pass H_2S for several minutes through the solution. A white precipitate of ZnS, soluble in excess HCl, indicates the presence of Zn^{++}.

Investigate the filtrate further for Groups III, II and I as described in 14.

9. Dissolving the Precipitated Sulphides and Separating Hg^{++}. Transfer the precipitate of Group IV sulphides to a porcelain basin, add a few drops of KNO_2 solution to accelerate the reaction, and boil *in the fume cupboard* with dilute (2 *N*) HNO_3. This dissolves all the sulphides with the exception of HgS**. The undissolved residue, which may contain HgS (black) or $Hg(NO_3)_2 \cdot 2HgS$ (white) and sulphur, is filtered off, washed, and investigated as described in 10. The filtrate, containing Cu^{++}, Cd^{++}, Bi^{+++} and Pb^{++} [the part not precipitated by HCl; see Sec. 66, 2, (c)] is investigated according to 11. It can also be investigated by the alkaline glycerol method described in Sec. 71 (4).

10. Detection of Hg^{++}. Transfer the precipitate to a porcelain basin and dissolve it on heating in the minimum amount of aqua regia (*in the fume cupboard*). Evaporate the solution down *cautiously* to about 1 ml (*not to dryness*, otherwise $HgCl_2$ will volatilize), dilute with water, filter, and test for Hg^{++} with $SnCl_2$. A white precipitate which is turned grey by excess stannous chloride ($Hg_2Cl_2 \rightarrow Hg$) indicates the presence of mercury.

The following alternative method can be used to detect Hg^{++}. Warm the precipitate with a mixture of 1-2 ml of concentrated HCl and a small amount of KI solution. This dissolves HgS to form $K_2[HgI_4]$. Filter off the residue. Boil the filtrate to remove H_2S, add a few drops of 2 *N* NH_4OH, cool, and add excess concentrated (25%) NaOH solution. A red-brown precipitate of



I indicates the presence of mercury.

* The test for Zn^{++} in the presence of HCl described on p. 304 may also be used, but it is first necessary to remove H_2S from the solution (see 14) and to oxidize Fe^{++} (formed as the result of reduction of Fe^{+++} by hydrogen sulphide) by boiling about 1 ml of the solution with 2-3 drops of concentrated HNO_3. If this is not done, Fe^{++} ions (which are not precipitated by $CaCO_3$) remain in solution and, after partial oxidation to Fe^{+++} by atmospheric oxygen, cause the precipitation of sulphur, resembling ZnS, when H_2S is passed.

** It should be remembered that the separation of Hg^{++} from the other Group IV cations is not sharp. A certain amount of HgS dissolves in HNO_3, especially if the precipitated sulphides were not washed quite free from Cl^- ions. The dissolved Hg^{++} subsequently occurs in the solution containing Cu^{++} and Cd^{++}. In the methods used for separating these ions (13, p. 373) Hg^{++} is precipitated as HgS together with Cu^{++} and does not interfere with detection of Cd^{++}.

11. Removal of Excess HNO_3 and Precipitation of Pb^{++}. To the solution from the separation of HgS (see 9) add a few millilitres of 2 *N* H_2SO_4 and evaporate in a porcelain basin (*in the fume cupboard*) until dense white fumes* of SO_3 appear. This removes HNO_3; in its presence Pb^{++} cannot be completely precipitated as $PbSO_4$, and it interferes with separation of Cu^{++} as metallic copper and with detection of Cd^{++} as CdS. At the same time all nitrates are converted into sulphates (because H_2SO_4 is less volatile of the two acids).

Cool the residue in the basin, and add cold water cautiously**.

If a precipitate of $PbSO_4$ is formed, filter it off. To confirm lead, the precipitate can be dissolved in 30% CH_3COONH_4 and tested for Pb^{++} with K_2CrO_4 or KI.

The solution, containing Cu^{++}, Cd^{++} and Bi^{+++} together with excess H_2SO_4, is investigated according to 12.

12. Separation and Detection of Bi^{+++}. Add NH_4OH to the solution in excess (until the liquid smells strongly of ammonia). This precipitates Bi^{+++} in the form of basic salts (white), while Cu^{++} and Cd^{++} remain in solution as the complexes $[Cu(NH_3)_4]^{++}$ and $[Cd(NH_3)_4]^{++}$. Filter off and wash the precipitate.

Test the precipitate for Bi^{+++} by reduction to the metal as follows. To 3-4 ml of 2 *N* NaOH solution add about 1/4 to 1/5 of its own volume of $SnCl_2$, to give a solution of sodium stannite, Na_2SnO_2. Pour this over the precipitate on the filter. Blackening indicates the presence of Bi^{+++} (p. 363).

Investigate the filtrate from the precipitation of Bi^{+++} as described in 13.

13. Detection of Cu^{++} and Cd^{++}. If the filtrate is blue, owing to the presence of the complex ion $[Cu(NH_3)_4]^{++}$, copper is present. If the colour is indistinct, acidify a separate portion of the filtrate with CH_3COOH and test for Cu^{++} by the more sensitive reaction with $K_4[Fe(CN)_6]$ (p. 357).

If Cu^{++} is absent, *slightly* acidify the ammoniacal solution with 2 *N* HCl and pass H_2S. A yellow precipitate of CdS indicates the presence of Cd^{++}.

In the presence of Cu^{++}, test for Cd^{++} as follows.

Slightly acidify the ammoniacal solution with 2 *N* HCl, heat, and pass H_2S to precipitate Cu^{++} and Cd^{++}. Filter off the precipitated sulphides of copper and cadmium and treat on the filter with 3-5 ml of 1 *N* HCl heated to boiling (this solution is prepared by mixing

---

* The SO_3 "fumes" (more correctly, mist) consist of minute droplets of H_2SO_4 formed when SO_3 comes into contact with water vapour in the air. They should not be confused with the paler HNO_3 vapour which is given off first. By the time the SO_3 fumes appear there is hardly any liquid left in the basin.

** $PbSO_4$ is soluble in concentrated sulphuric acid, and is precipitated only when the solution is diluted with water.

1. Preliminary tests for NH_4^+, Fe^{++} and Fe^{+++}

2. Separation of the first subgroup of Group IV by HCl

Precipitate: AgCl, $PbCl_2$ (part), $PbSO_4$, Hg_2Cl_2, BiOCl, Group II sulphates

3. Treat with hot water

Precipitate: AgCl, $PbSO_4$, Hg_2Cl_2, BiOCl, Group II sulphates

4. Treat precipitate with NH_4OH solution

Solution: $PbCl_2$ Test for Pb^{++}

Precipitate: $[HgNH_2]Cl + Hg$ (black), $PbSO_4$, BiOCl, Ag, Group II sulphates

6. Treat precipitate with CH_3COONH_4 solution

Solution: $[Ag(NH_3)_2]Cl$ **5.** Test for Ag^+

Precipitate: $PbSO_4$ (part), BiOCl, $[HgNH_2]Cl$ (part) *, Hg, Ag, and Group II sulphates

7. Dissolve BiOCl in hot 2 *N* HCl

Solution: Pb^{++} Test for Pb^{++}

Precipitate: $PbSO_4$ $[HgNH_2]Cl$ (part), Hg, Ag, Group II sulphates. Test for silver (see 7,a) and for Group II sulphates (see 7,b)

Solution: Bi^{+++} (HCl). Added to solution obtained by the action of HCl in 2

* A considerable amount of $[HgNH_2]Cl$ dissolves when the precipitate is treated with CH_3COONH_4 (according to 6)

Table 23

Groups IV-I Cations

Solution: Pb^{++} (part), Hg^{++}, Cu^{++}, Cd^{++}, Bi^{+++}, Groups III, II and I cations (HCl)

8. Adjust the acidity and precipitate the second subgroup of Group IV by H_2S

Precipitate: PbS, HgS, CuS, CdS, Bi_2S_3

9. Treat precipitate with hot dilute HNO_3

Precipitate: HgS (black) or $Hg(NO_3)_2 \cdot 2HgS$ (white) and S

10. Test for Hg^{++}

Solution: Pb^{++}, Cu^{++}, Cd^{++}, Bi^{+++} (HNO_3)

11. Evaporate with H_2SO_4 until SO_3 fumes appear to remove HNO_3 and to precipitate Pb^{++}. Dilute with water

Precipitate: $PbSO_4$ Dissolve in CH_3COONH_4 and test for Pb^{++}

Solution: Cu^{++}, Cd^{++}, Bi^{+++} (H_2SO_4)

12. Separate Bi^{+++} by means of NH_4OH

Precipitate: basic Bi salts. Test for Bi^{+++}

Solution: $[Cu(NH_3)_4]^{++}$ $[Cd(NH_3)_4]^{++}$

13. Test for Cu^{++}. Acidify with HCl and precipitate Cu^{++} and Cd^{++} by H_2S. Treat the precipitate (CuS + CdS) with hot 1 *N* HCl

Precipitate: CuS, not investigated

Solution: Cd^{++}(HCl). Test for Cd^{++} (dilute with water, pass H_2S)

Solution: Groups III, II and I cations (HCl, H_2S). Test for Zn^{++} by action of H_2S in presence of formate buffer (see 8).

14. Boil out H_2S, filter off precipitated sulphur. Evaporate and investigate the solution according to Table 18 (p. 309)

of the 2 *N* acid with an equal volume of water*). This dissolves CdS while copper sulphide, which has a much lower solubility product, remains on the filter. Dilute the filtrate with twice its own volume of water and test for Cd^{++} by the action of H_2S.

14. Preparation of the Solution for Detection of Groups III, II and I Cations. Boil the filtrate obtained after separation of Group IV sulphides (see 8) *in the fume cupboard* to remove H_2S, filter off the precipitated sulphur, and evaporate to about 20 ml. Test the solution for Groups III, II and I as described on pp. 304 *et seq.*

ALKALINE GLYCEROL PROCEDURE FOR ANALYSIS OF THE SECOND SUBGROUP OF GROUP IV

1. Separation of Cd^{++} from Cu^{++}, Bi^{+++} and Pb^{++}. Add glycerol diluted with water (1 : 1) to the nitric acid solution obtained when the Group IV sulphides were dissolved (see 9). Add 6 *N* NaOH drop by drop until the solution is just alkaline, followed by 8-10 more drops. Mix the contents of the test tube thoroughly.

Any Cu^{++}, Bi^{+++} and Pb^{++} ions form complex compounds with glycerol and remain in solution, while Cd^{++} is precipitated as $Cd(OH)_2$. Heat the solution for 1 minute, filter off the precipitate and wash it twice with 2 *N* alkali solution containing glycerol (2-3 drops to 20 drops of alkali) to remove hydroxides of other metals (especially bismuth). Finally wash once with water and investigate according to 2. Investigate the filtrate as described in 3.

2. Detection of Cd^{++}. Dissolve the washed precipitate in 2 *N* HCl, dilute the solution with water, and pass H_2S. A yellow precipitate of CdS indicates the presence of Cd^{++}.

Note. If the CdS precipitate is darkish rather than bright yellow, owing to incomplete removal of coprecipitated bismuth and copper hydroxide during washing with NaOH, it should be filtered off and treated with hot HCl as described in Sec. 71 (p. 360, c). Dilute the solution with a large amount of water and test for Cd^{++} by the action of H_2S, which precipitates CdS of the characteristic lemon-yellow colour.

3. Detection of Cu^{++}, Pb^{++}, and Bi^{+++}. Test for Cu^{++}, Pb^{++}, and Bi^{+++} in separate portions of the solution.

(a) Cu^{++}. A blue colour indicates the presence of Cu^{++}. If the colour is indistinct or absent, acidify a part of the filtrate with CH_3COOH and add $K_4[Fe(CN)_6]$ solution. A reddish brown precipitate of $Cu_2[Fe(CN)_6]$ indicates the presence of Cu^{++}.

---

* It is useful to re-heat the filtered solution and to use it for treating the precipitate on the filter again.

(b) Pb^{++}. Acidify another portion of the filtrate dropwise with concentrated CH_3COOH solution and add K_2CrO_4. A yellow precipitate of $PbCrO_4$, soluble in caustic alkali, indicates* the presence of Pb^{++}.

(c) Bi^{+++}. Add 4-5 ml of 2 *N* NaOH to 1 ml of $SnCl_2$ and mix; sodium stannite, Na_2SnO_2, is formed. Add the unknown alkaline solution to it.

In the presence of Bi^{+++}, black metallic bismuth is precipitated.

QUESTIONS AND PROBLEMS

1. How does Group IV differ from (a) Groups I and II; (b) Group III?
2. How is Group IV separated into subgroups?
3. Explain why, unlike the Group III sulphides, Group IV sulphides do not dissolve in dilute HCl and H_2SO_4. What is the action of HNO_3 on them? Write the equations for the reactions of HNO_3 with the sulphides of copper and bismuth. How can mercuric sulphide be dissolved? Write the equation for this reaction.
4. What cations are precipitated by ammonium sulphide from a solution containing all the cations of Groups I, II, III and IV?
5. Explain why the solution is acidified before precipitation of the second subgroup of Group IV by H_2S.
6. Explain why the following acids are unsuitable for acidifying the solution before precipitation of Group IV by hydrogen sulphide: (a) sulphuric; b) nitric; (c) acetic.
7. What should the H^+ ion concentration be for precipitation of Group IV cations by hydrogen sulphide? Explain what errors could arise during the analysis if the acidity of the solution during precipitation was (a) too high; (b) too low.
8. Explain why a hot solution is used at first during precipitation by hydrogen sulphide. Why is it subsequently diluted with cold water?
9. Explain why the precipitated Group IV sulphides must be filtered off without delay.
10. What is the action of ammonia solution on AgCl? How can Ag^+ be detected in the solution formed?
11. What is the action of NH_4OH on Hg_2Cl_2?
12. Compare the effects of ammonia and potassium cyanide solutions on silver chloride, bromide and iodide respectively, and explain the difference.
13. Describe how (a) $PbCl_2$; (b) $PbSO_4$; (c) basic bismuth (or antimony and tin) salts are separated from the other substances precipitated.
14. Excess of (a) caustic alkali, (b) ammonia solution is added to a mixture of nitrates of all the Group IV cations. State what compounds will be present in the solution and the precipitate in each case, and illustrate your answer by equations.
15. Why does H_2S precipitate the corresponding sulphide from complex cadmium cyanide but not from the analogous copper compound?
16. Describe the principle of the alkaline glycerol method of analysis of the second subgroup of Group IV.

---

* If insufficient acetic acid is present, yellow bismuthyl chromate may be precipitated; this is indistinguishable in appearance from $PbCrO_4$, but it is insoluble in caustic alkali and dissolves in concentrated acetic acid.

17. What happens when solutions of bismuth chloride and nitrate are diluted with water?

18. What reactions are used (a) for detection of Bi^{+++}, (b) for separating Bi^{+++} from Cu^{++} and Cd^{++}?

19. Explain why, in analysis of the second subgroup of Group IV, the solution must be evaporated until SO_3 "fumes" appear. What are these "fumes" and what does their appearance indicate?

20. Describe the detection and separation of Cu^{++} and Cd^{++} ions, and explain the principle of the separation.

21. How is Hg^{++} detected and separated from the other Group IV cations?

22. A mixture contains the solid salts $AgNO_3$, $CuSO_4$, $FeCl_3$ and $KMnO_4$. Describe the processes which occur when it is dissolved in water and subsequently analyzed; illustrate your answer by equations.

CHAPTER VI

CATIONS OF GROUP V

74. General Characteristics of Group V Cations. Thiosalts

Analytical Group V contains the ions of arsenic, antimony and tin. In the method adopted in this book for separating Groups IV and V, bivalent mercury is also found in Group V*.

The sulphides of these metals have low solubility products. Like the Group IV sulphides, *they are insoluble in dilute acids and are precipitated by hydrogen sulphide in acid solution* (at pH = 0.5).

The difference between Groups IV and V is that the sulphides of the latter are soluble in Na_2S, K_2S *or* $(NH_4)_2S$ *to form thiosalts, e.g.,*

$$SnS_2 + Na_2S = Na_2SnS_3$$

Sodium thiostannate

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3 \quad \text{etc.}$$

Ammonium thioarsenite

In the ionic form, these reactions are:

$$SnS_2 + S^{--} = SnS_3^{--}$$

$$As_2S_3 + 3S^{--} = 2AsS_3^{---}$$

Thiosalts are the salts of the corresponding thioacids, such as thiostannic H_2SnS_3, thioarsenious H_3AsS_3, etc. These acids are similar in composition to the corresponding oxyacids, but the oxygen atoms are replaced by atoms of an analogous element, sulphur; for example:

arsenious acid	H_3AsO_3	— thioarsenious acid	H_3AsS_3
arsenic acid	H_3AsO_4	— thioarsenic acid	H_3AsS_4
antimonous acid	H_3SbO_3	— thioantimonous acid	H_3SbS_3
antimonic acid	H_3SbO_4	— thioantimonic acid	H_3SbS_4
stannic acid	H_2SnO_3	— thiostannic acid	H_2SnS_3

Correspondingly, the above reactions of thiosalt formation are similar to the reaction in which salts of oxyacids are formed from acidic and basic oxides. For example, the reaction

$$SnS_2 + Na_2S = Na_2SnS_3$$

---

* For the reactions of Hg^{++}, see Sec. 69.

is similar to the reaction

$$SnO_2 + Na_2O = Na_2SnO_3$$

This comparison shows that, *in contrast to sulphides of Groups I-IV, the sulphides of Group V are distinctly acidic.* They can be described as the thioanhydrides of thioacids because the latter form the corresponding sulphides when they liberate H_2S, just as oxyacids can lose water to form anhydrides, e.g.,

$$H_2SnO_3 = H_2O + SnO_2 \qquad H_2SnS_3 = H_2S + SnS_2$$
$$2H_3AsO_3 = 3H_2O + As_2O_3 \qquad 2H_3AsS_3 = 3H_2S + As_2S_3$$

The acidic nature of Group V sulphides is associated with the position of the corresponding elements in the periodic system. They are in Groups IV (Sn) and V (As and Sb) of the periodic system, in the second half of the long periods. The elements located here exhibit non-metallic properties which are manifested in the acidic nature of their oxides and sulphides. In accordance with the general rule, the acidic nature should be most pronounced in the Group V elements, As and Sb, especially in their highest oxidation states, i.e., in the compounds As_2S_5 and Sb_2S_5. The acidic nature of the Group IV element, Sn, is less pronounced and appears only in compounds of the highest oxidation state, such as SnS_2. The sulphides of bivalent tin, SnS, is a basic sulphide and therefore does not form thiosalts with Na_2S and $(NH_4)_2S$.

Consequently *in separating Group V from Group IV it is necessary to oxidize* Sn^{++} *ions to* Sn^{++++} *by some means.*

The structure of the outer electron shells of the ions of analytical Group V is the same as that of Group IV cations. Group V includes ions which have: (a) an outer shell of 18 or (18 + 2) electrons; (b) an incomplete outer shell, i.e., transitional from 8 to 18 electrons. provided that internal shells of 18 or 32 electrons are present; the presence of these intensifies both the polarizing action and the polarizability of the ions.

It is because of the similar structure of the outer electron shells that Group IV and V ions behave similarly with hydrogen sulphide in acid solution, i.e., form sulphides with very small solubility products. The chemical difference between the sulphides on which the subdivision of analytical Groups IV and V is based can be, according to the researches of N. I. Blok, correlated with the *ionic potentials* of the cations of these groups.

The ionic potential is the ratio of the charge of an ion to its effective radius, Z/R. The ionic potential can be regarded as a rough measure of the strength of the electric field of the ion. In some cases, as for comparison of the acid-base properties of ions *with the same external electron structure*, the ionic potential can serve as an approximate criterion of such properties. For example, Table 24 shows that with the same external electron structure ions with low values of the ionic potential Z/R form basic sulphides; therefore they are included in analytical Group IV. Conversely, ions with large Z/R form acidic

Table 24

Effect of the Ionic Potential Z/R on the Chemical Nature of Sulphides Formed by Ions of Groups IV and V

Ions	Structure of outer electron shell	Ionic potential Z/R	Chemical nature of sulphide	Analytical group
Au^{+}, Ag^{+}, Cu^{+}, Hg^{++}, Cd^{++} (Zn^{++}) *	18 electrons	0.7-2.4	Basic	IV
Sn^{IV}, Ge^{IV}, Sb^{V}, As^{V}	18 electrons	5.4-10.6	Acidic	V
Pb^{++}, Sn^{++}, Bi^{+++}	18+2 electrons	1.5-2.9	Basic	IV
Sb^{III}, As^{III}	18+2 electrons	3.3-4.4	Acidic	V

* The Zn^{++} cation, which on practical grounds is included in analytical Group III (see p. 35), is in reality intermediate between Group III and Group IV, both by the structure of its outer electron shell and its position in the periodic system, and by the fact that it is precipitated by hydrogen sulphide in acid solutions (pH = 2).

sulphides (thioanhydrides), which dissolve in caustic alkalies and in solutions of alkali-metal sulphides [Na_2S, $(NH_4)_2S$, etc.] to form thiosalts. Therefore they are included in analytical Group V.

From all that has been said about the properties of Group V sulphides, it follows that two different operations are needed to separate them from the other groups:

(a) separation from cations of Groups III, II and I by the action of hydrogen sulphide in acid solution (pH = 0.5); cations of the second subgroup of Group IV are precipitated together with Group V;

(b) separation from Group IV by treatment of the mixture of Group IV and V sulphides (formed by precipitation with H_2S) with any reagent which acts on Group V sulphides to form thiosalts. Group IV sulphides remain in the precipitate and are thus separated from Group V.

Since Group V ions are finally isolated from mixtures with cations of other groups only after the second of these operations, the reagent which dissolves Group V sulphides to form thiosalts is regarded as the group reagent. Various substances are used for this purpose in analytical practice. For example, ammonium polysulphide*, $(NH_4)_2S_2$

* Polysulphides are salts corresponding to various polysulphides of hydrogen—H_2S_2, H_2S_3, etc. The reagent used in practice does not exactly correspond to the formula $(NH_4)_2S_2$, but is a mixture of various polysulphides from $(NH_4)_2S_2$ to $(NH_4)_2S_9$. It is prepared by dissolving sulphur in ammonium sulphide, $(NH_4)_2S$, and always contains an excess of the latter.

s often used. This compound has the advantage that, being an oxi-lizing agent, it first oxidizes SnS to SnS_2 and the latter then lissolves to form a thiosalt:

$$SnS + (NH_4)_2S_2 = SnS_2 + (NH_4)_2S$$
$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

However, $(NH_4)_2S_2$ has the following disadvantages:

(a) CuS and HgS are partially dissolved;

(b) the precipitated sulphides are strongly contaminated with ;ulphur, which is formed by decomposition of excess $(NH_4)_2S_2$ when .he solution is subsequently acidified:

$$(NH_4)_2S_2 + 2CH_3COOH = 2CH_3COONH_4 + H_2S\uparrow + \downarrow S$$

(c) when $(NH_4)_2S_2$ is used, the mixture obtained is often difficult ;o filter.

Because of all this, we will use *sodium sulphide*, Na_2S (*containing* NaOH *to suppress hydrolysis*), *as the group reagent for Group V.*

In comparison with ammonium sulphide, which is hydrolyzed ılmost completely in aqueous solutions, sodium sulphide is hydro-yzed far less (especially in the presence of caustic soda), being a ;alt of the same acid (H_2S) but of a stronger base. Therefore Na_2S solution has a much higher concentration of S^{--} ions than ;olutions of $(NH_4)_2S$ or $(NH_4)_2S_2$.

However, HgS also dissolves with formation of a thiosalt in solu-;ions of high S^{--} concentrations:

$$HgS + Na_2S = Na_2HgS_2 \text{ or } HgS + S^{--} = HgS_2^{--}$$

Therefore Na_2S completely dissolves Hg^{++} ions in the form of HgS_2^{--} anions, which pass into the solution containing thiosalts of :he Group V elements. On the other hand, when $(NH_4)_2S_2$ is used ıs the group reagent, Hg^{++} remains in the precipitate together with :he Group IV cations*.

It is obvious that, as in the case of oxides, a sharp boundary can-not be drawn between basic and acidic sulphides, because some of :hem behave differently under different conditions.

The elements As, Sb, and Sn all exist in two states of oxidation:

As_2O_3	As_2O_5	Sb_2O_3	Sb_2O_5	SnO	SnO_2
Arsenious anhydride	Arsenic anhydride	Antimonous anhydride	Antimonic anhydride	Stannous oxide	Stannic oxide

* Sometimes NaOH or KOH is used as the group reagent for Group V, ıs these compounds readily dissolve the sulphides of arsenic, antimony, and ;tannic tin, but not Group IV sulphides. However, they have the disadvantage that HgS may partially dissolve and partially remain in the precipitate.

In accordance with the positions of the elements in the periodic system, their hydroxides are sometimes (Sn) closer to bases, and sometimes (As, Sb) are more like acids, but they always combine the properties of both, i.e., they are of amphoteric character to some degree. For example, stannous hydroxide, $Sn(OH)_2$ (or H_2SnO_2), dissolves both in acids and in alkalies (in the latter case to form stannites):

$$Sn(OH)_2 + 2H^+ = Sn^{++} + 2H_2O$$
$$H_2SnO_2 + 2OH^- = SnO_2^{--} + 2H_2O$$

Thus, in acid solutions bivalent tin is present mainly in the form of Sn^{++} cations whereas in alkaline solutions it yields, in accordance with dissociation of stannites, mainly SnO_2^{--} anions. Similarly, quadrivalent tin can exist in solution either as Sn^{++++} cations, or more correctly as complex $[SnCl_6]^{--}$ ions (in acidified $SnCl_4$ solutions), or as SnO_3^{--} anions (in stannates, which are salts of metastannic acid, H_2SnO_3).

The corresponding arsenic and antimony compounds are of a somewhat similar character. Arsenic, being an element of the odd series of Group V in the periodic system, is much closer to non-metals than to metals. Its oxides As_2O_3 and As_2O_5 correspond to arsenous acid H_3AsO_3 and arsenic acid H_3AsO_4. These acids and their salts (arsenites and arsenates) are the commonest compounds of arsenic, and in analysis we are usually concerned with AsO_3^{---} and AsO_4^{---} anions. However, since arsenic can be precipitated by hydrogen sulphide in the form of sulphides, it is reasonable to suppose that because of the amphoteric nature of the corresponding hydroxides, H_3AsO_3 and H_3AsO_4, solutions of arsenic salts also contain As^{+++} and As^{+++++} in equilibrium with these cations (Sec. 45). For example:

$$AsO_3^{---} + 6H^+ \rightleftarrows As^{+++} + 3H_2O$$

However, the As^{+++} concentration in neutral solutions of arsenites is so low that the solubility product of As_2S_3 is not reached in the presence of H_2S and a precipitate is not formed.

If the solution is acidified, the equilibrium shifts to the right and As_2S_3 is precipitated.

Antimony behaves similarly to arsenic. Because of this action of H_2S on arsenic and antimony ions, they can be included with the cations rather than with the anions.

It follows from the above that Group V ions are precipitated by hydrogen sulphide in acid solutions only. In addition to shifting the equilibrium towards formation of As^{+++}, Sb^{+++}, etc., cations, addition of acid also helps to coagulate Group V sulphides, which have a strong tendency to form colloidal solutions.

Hydrogen sulphide does not precipitate Group V sulphides in neutral or acid solutions. Obviously, they are not precipitated by excess $(NH_4)_2S$ or Na_2S either, as solutions of the corresponding thiosalts are formed.

In contrast to Group V, the sulphides of Group IV are precipitated both by hydrogen sulphide and by its soluble salts.

75. Action of the Group Reagent

The final separation of Group V from cations of the other groups is achieved not by precipitation in the form of insoluble compounds, but by treatment of the mixture of Group IV and V sulphides with Na_2S solution, which dissolves Group V sulphides while Group IV sulphides remain in the residue. Therefore Na_2S is regarded as the group reagent for this group.

Study experimentally the preparation and properties of Group V sulphides; first, examine the action of sodium sulphide on them.

1. Arsenic. *a. Trivalent Arsenic.* To 4-5 ml of Na_3AsO_3 or K_3AsO_3 (*highly poisonous*) solution add HCl until acid and pass H_2S through the solution. Yellow As_2S_3 is precipitated.

The reaction can be represented by the equations:*

$$2AsO_3^{---} + 12H^+ \rightleftarrows 2As^{+++} + 6H_2O$$

$$2As^{+++} + 3H_2S = As_2S_3 + 6H^+$$

$$2AsO_3^{---} + 6H^+ + 3H_2S = \downarrow As_2S_3 + 6H_2O$$

In the molecular form the equation is

$$2Na_3AsO_3 + 6HCl + 3H_2S = \downarrow As_2S_3 + 6NaCl + 6H_2O$$

Filter off the precipitated As_2S_3 and divide it into four portions. Leave one for further experiments (the action of HNO_3; see below), and add Na_2S to the second, NaOH or NH_4OH to the third, and $(NH_4)_2CO_3$ to the fourth.

In every case the precipitate dissolves**:

$$As_2S_3 + 3Na_2S = 2Na_3AsS_3$$

$$As_2S_3 + 6NaOH = Na_3AsS_3 + Na_3AsO_3 + 3H_2O$$

$$As_2S_3 + 3(NH_4)_2CO_3 = (NH_4)_3AsS_3 + (NH_4)_3AsO_3 + 3CO_2 \uparrow$$

Write the ionic equations for these reactions.

When the precipitate is dissolved in alkalies, the arsenite ion AsO_3^{---} is formed in addition to AsS_3^{---}. A very important property of As_2S_3 (and As_2S_5) is solubility in $(NH_4)_2CO_3$; this distinguishes

* See Sec. 74.

** Keep the solutions for further experiments.

them from the other Group V sulphides. This property can be used for separating arsenic in analysis. The reason for this difference is that, at a relatively low pH of 9.13 (see Table 15, p. 216) created by ammonium carbonate, only sulphides with the most pronounced acidic properties can form thiosalts. Arsenic, being an element in the odd series of Group V of the periodic system, and of a lower atomic weight than antimony, forms sulphides which are the most acidic of all the sulphides in question.

Another important distinction of arsenic sulphides is that they are insoluble in concentrated HCl; we will use this property for separating arsenic from antimony and tin in analysis. As_2S_3 can be dissolved in concentrated HNO_3 or in aqua regia. Confirm this experimentally with the remaining portion of the As_2S_3 precipitate; add the acid or aqua regia and heat.

In the case of HNO_3 the reaction is*:

$$3As_2S_3 + 28HNO_3 + 4H_2O = 6H_3AsO_4 + 9H_2SO_4 + 28NO\uparrow$$

or

$$3As_2S_3 + 10H^+ + 28NO_3^- + 4H_2O = 6H_3AsO_4 + 9SO_4^{--} + 28NO\uparrow$$

As_2S_3 is also readily converted into AsO_4^{---} ions by heating with a mixture of hydrogen peroxide and alkali or ammonium carbonate, e.g.:

$$As_2S_3 + 14H_2O_2 + 6(NH_4)_2CO_3 = 2(NH_4)_3AsO_4 + 3(NH_4)_2SO_4 + 14H_2O + 6CO_2\uparrow$$

A very important general property of thiosalts is that they are decomposed by acids with formation of precipitated sulphides. Carry out this reaction with the Na_3AsS_3 solution obtained by the action of Na_2S on arsenious sulphide.

The action of acids on thiosalts is due to the instability of free thioacids, which decompose immediately to give thioanhydrides and H_2S as soon as they have been formed from their salts. For example:

$$2Na_3AsS_3 + 6HCl = 2H_3AsS_3 + 6NaCl$$

$$2H_3AsS_3 = \downarrow As_2S_3 + 3H_2S\uparrow$$

or, in ionic form

$$2AsS_3^{---} + 6H^+ = \downarrow As_2S_3 + 3H_2S\uparrow$$

The following reaction occurs when an acid acts on the mixture of arsenite and thioarsenite obtained by treatment of the As_2S_3 precipitate with alkali or with ammonium carbonate:

$$AsS_3^{---} + AsO_3^{---} + 6H^+ = \downarrow As_2S_3 + 3H_2O$$

---

* The derivation of this equation is given on p. 246.

b. Quinquevalent Arsenic. In moderately acid solutions of arsenates, such as Na_2HAsO_4 (*highly poisonous*) hydrogen sulphide does not give a precipitate for a long time in the cold. Gradually the liquid becomes turbid and eventually yellow As_2S_3 is precipitated.

The explanation of this reaction is that H_3AsO_4 is a much stronger acid and a much weaker base than H_3AsO_3. Therefore the equilibrium

$$AsO_4^{---} + 8H^+ \rightleftarrows As^{+++++} + 4H_2O$$

is shifted far to the left. In a moderately acid solution an As^{+++++} ion concentration sufficient to exceed the solubility product of As_2S_5 cannot be obtained, and therefore the latter is not precipitated by H_2S. At the same time H_2S, in accordance with the position of the S/S^{--} couple in the table of oxidation potentials ($E_0 = -0.51$ V), can reduce the AsO_4^{---} ion ($E_0 = +0.57$ V) to AsO_3^{---}:

$$AsO_4^{---} + H_2S = AsO_3^{---} + H_2O + \downarrow S$$

We saw earlier that, in contrast to AsO_4^{---}, the AsO_3^{---} ion yields a sufficient quantity of As^{+++} cations in the presence of acids; therefore the following reaction should occur as the reduction proceeds:

$$2AsO_3^{---} + 6H^+ + 3H_2S = \downarrow As_2S_3 + 6H_2O$$

Multiplying the first equation by 2 and adding it to the second, we obtain the overall equation for the reaction:

$$2AsO_4^{---} + 6H^+ + 5H_2S = \downarrow As_2S_3 + \downarrow 2S + 8H_2O$$

The reduction of AsO_4^{---} to AsO_3^{---} by hydrogen sulphide is very slow. To accelerate it, the solution is heated to about 70° for the precipitation. It is also helpful to add one or two drops of NH_4I solution* as a catalyst. This catalyst acts as follows. Iodide ions reduce AsO_4^{---} ions *rapidly* to AsO_3^{---}:

$$AsO_4^{---} + 2I^- + 2H^+ = AsO_3^{---} + I_2 + H_2O$$

However, I_2 ($E_0 = +0.54$ V) is considerably below the S/S^{--} couple in the table of oxidation potentials, and as soon as it is formed it reacts with H_2S, being itself reduced back to I^- ions:

$$I_2 + H_2S = 2I^- + 2II^+ + \downarrow S$$

Thus, I^- ions are completely regenerated and are not consumed in the reaction; but the reaction is considerably accelerated in their presence, as it proceeds by the stages shown above, which are much more rapid than direct interaction between AsO_4^{---} and H_2S.

* If NH_4I is not available, an alcoholic solution of iodine may be used. Hydrogen sulphide immediately reduces I_2 to I^- ions.

It is also possible to obtain As_2S_5 by the action of H_2S on a salt of H_3AsO_4 if the precipitation is performed in the cold* by a rapid stream of H_2S in the presence of excess concentrated HCl. The latter favours conversion of AsO_4^{---} anions into As^{+++++} cations. The reaction is relatively rapid. The sulphide of quinquevalent arsenic is a yellow precipitate which reacts in the same way as As_2S_3 with all the above-mentioned reagents. For example,

$$As_2S_5 + 3Na_2S = 2Na_3AsS_4$$

$$As_2S_5 + 3(NH_4)_2CO_3 = (NH_4)_3AsS_4 + (NH_4)_3AsO_3S + 3CO_2 \uparrow$$

$(NH_4)_3AsO_3S$ is known as an oxy-thiosalt; it differs from $(NH_4)_3AsO_4$ in that one oxygen atom in the molecule is replaced by sulphur.

Alkalies also form oxythiosalts with As_2S_5:

$$As_2S_5 + 6NaOH = Na_3AsS_4 + Na_3AsO_3S + 3H_2O$$

or

$$As_2S_5 + 6OH^- = AsS_4^{---} + AsO_3S^{---} + 3H_2O$$

2. Antimony. Hydrochloric acid solutions of $SbCl_3$ and $SbCl_5$ predominantly contain the complex ions $[SbCl_6]^{---}$ and $[SbCl_6]^-$. The action of H_2S on them in the presence of HCl is represented by the equations:

$$2[SbCl_6]^{---} + 3H_2S = \downarrow Sb_2S_3 + 6H^+ + 12Cl^-$$

$$2[SbCl_6]^- + 5H_2S = \downarrow Sb_2S_5 + 10H^+ + 12Cl^-$$

The colour of the precipitates is orange-red. They dissolve in Na_2S and in caustic alkalies, but not in $(NH_4)_2CO_3$ (distinction from As); for example:

$$Sb_2S_5 + 3Na_2S = 2Na_3SbS_4$$

$$Sb_2S_5 + 6NaOH = Na_3SbS_4 + Na_3SbO_3S + 3H_2O$$

Antimony thiosalts are decomposed by acids; e.g.,

$$2Na_3SbS_4 + 6CH_3COOH = \downarrow Sb_2S_5 + 6CH_3COONa + 3H_2S \uparrow$$

In contrast to arsenic sulphides, antimony sulphides dissolve in concentrated HCl on heating. Sb^V is reduced to Sb^{III}:

$$Sb_2S_5 + 12HCl = 2H_3[SbCl_6] + 3H_2S \uparrow + \downarrow 2S$$

3. Tin. Dark brown SnS is precipitated by the action of H_2S on $SnCl_2$ solution in the presence of HCl. In contrast to the other Group

---

* On heating a part of the AsO_4^{---} ions is reduced to AsO_3^{---}, and a mixture of As_2S_3 and As_2S_5 is formed.

V sulphides, SnS *is basic and does not dissolve in* Na_2S. On the other hand, it dissolves in $(NH_4)_2S_2$, because SnS is oxidized by the polysulphide to SnS_2, which forms a thiosalt (p. 382).

When H_2S is passed through $SnCl_4$ solution acidified with HCl, containing complex $[SnCl_6]^{--}$ ions, a yellow precipitate of SnS_2 is formed. It is soluble in Na_2S and alkalies but not in $(NH_4)_2CO_3$ (distinction from As):

$$SnS_2 + Na_2S = Na_2SnS_3$$

Tin thiosalts are decomposed by acids with formation of stannic sulphide.

Like the sulphides of antimony, SnS_2 dissolves when heated with concentrated hydrochloric acid to form the complex chlorostannic acid $H_2[SnCl_6]$ (distinction from arsenic):

$$SnS_2 + 6HCl = H_2[SnCl_6] + 2H_2S\uparrow$$

4. Mercury. The Hg^{++} ion gives a black precipitate of HgS with H_2S (Sec. 66). Its characteristic feature is that it is *insoluble* in HNO_3 (distinction from all the other Group IV and V sulphides). This fact is often used for separating mercuric sulphide from the sulphides of Group IV.

HgS can be dissolved in aqua regia or in a mixture of concentrated HCl and KI solutions. The latter reaction is:

$$HgS + 2HCl + 4KI = K_2[HgI_4] + 2KCl + H_2S\uparrow$$

or

$$HgS + 2H^+ + 4I^- = [HgI_4]^{--} + H_2S\uparrow$$

Mercuric sulphide is intermediate in properties between the sulphides of Groups IV and V. Like the Group IV sulphides, HgS is insoluble in $(NH_4)_2S$ and $(NH_4)_2S_2$, as solutions of these compounds are extensively hydrolyzed with formation of HS^- ions and have relatively small amounts of S^{--} ions. Sodium sulphide, on the other hand, is hydrolyzed much less and it dissolves mercuric sulphide. A thiosalt is formed:

$$HgS + Na_2S = Na_2HgS_2$$

Like the thiosalts of other Group V elements, the mercury thiosalt is decomposed by acids and HgS is precipitated:

$$Na_2HgS_2 + 2HCl = \downarrow HgS + 2NaCl + H_2S\uparrow$$

or

$$HgS_2^{--} + 2H^+ = \downarrow HgS + H_2S\uparrow$$

As we use Na_2S for separating Groups IV and V, Hg^{++} ion belongs to Group V.

76. Reactions of Arsenic Ions

As already stated, trivalent arsenic exists in solution mainly in the form of AsO_3^{---} or AsO_2^- (metaarsenite) ions. When solutions containing these ions are acidified, appreciable amounts of As^{+++} cations are formed.

Quinquevalent arsenic forms AsO_4^{---} (or $HAsO_4^{--}$) anions almost exclusively. All these ions are colourless.

Arsenic compounds are highly poisonous!

Reactions of the arsenite ion, AsO_3^{---}

1. **Silver nitrate,** $AgNO_3$, gives a yellow precipitate of Ag_3AsO_3 with the AsO_3^{---} ion:

$$AsO_3^{---} + 3Ag^+ = \downarrow Ag_3AsO_3$$

The precipitate dissolves in HNO_3 and in NH_4OH. In the latter case the complex ion $[Ag(NH_3)_2]^+$ is formed.

2. **Iodine solution,** I_2, oxidizes AsO_3^{---} to AsO_4^{---}, and the brown colour of the iodine solution disappears. The reaction is

$$AsO_3^{---} + I_2 + H_2O \rightleftarrows AsO_4^{---} + 2I^- + 2H^+$$

(disappearance of the brown colour characteristic of iodine solutions).

As the oxidation potential of the AsO_4^{---}/AsO_3^{---} couple ($E_0 = +0.57$ V) is higher than that of the $I_2/2I^-$ couple ($E_0 = +0.54$ V) the reaction tends to go from right to left. To shift the equilibrium in the opposite direction, $NaHCO_3$ is added to remove H^+ ions; this lowers the oxidation potential of the AsO_4^{---}/AsO_3^{---} couple below that of the $I_2/2I^-$ couple (Sec. 63).

Add a small amount of solid* $NaHCO_3$ to $NaAsO_2$ solution; when it has dissolved, add iodine solution drop by drop. Note the disappearance of the iodine colour.

The AsO_3^{---} anion can reduce other oxidizing agents, such as solutions of chlorine, bromine, etc.

Reactions of the arsenate ion, AsO_4^{---}

1. **Silver nitrate,** $AgNO_3$, forms a characteristic chocolate-brown (distinction from AsO_3^{---}) precipitate of Ag_3AsO_4 with the AsO_4^{---} ion; the precipitate is soluble in HNO_3 and NH_4OH:

$$3Ag^+ + AsO_4^{---} = \downarrow Ag_3AsO_4$$

---

* Na_2CO_3 cannot be used, as it decolourizes I_2 even in the absence of AsO_3^{---}

$$3I_2 + 3Na_2CO_3 = NaIO_3 + 5NaI + 3CO_2 \uparrow$$

2. Potassium iodide, KI, is oxidized by arsenate ions to free I_2 and the solution turns brown:

$$AsO_4^{---} + 2I^- + 2H^+ \rightleftarrows AsO_3^{---} + I_2 + H_2O$$

This is the reverse of the reaction between I_2 and AsO_3^{---} ions discussed above; to shift the equilibrium to the right the H^+ ion concentration must be increased as far as possible rather than decreased.

Accordingly, carry out this reaction in the presence of concentrated HCl.

If benzene, in which I_2 is more soluble than in water, is added to the solution and the liquid is shaken, most of the iodine passes into the benzene layer, which acquires a characteristic violet colour.

3. Magnesium salts in the presence of NH_4OH and NH_4Cl give a white crystalline precipitate of $MgNH_4AsO_4$, soluble in acids but almost insoluble in 2.5% ammonia solution:

$$MgCl_2 + NH_4OH + Na_2HAsO_4 = \downarrow MgNH_4AsO_4 + 2NaCl + H_2O$$

The reaction is analogous to the reaction of the Mg^{++} ion studied earlier (p. 100), except that it involves the AsO_4^{---} ion instead of the very similar PO_4^{---} ion.

To carry out this reaction, mix the arsenate solution with an equal volume of magnesia mixture* and leave the solution to stand if necessary.

4. Ammonium molybdate solution (solution of $(NH_4)_2MoO_4$ in HNO_3) forms with arsenate solutions a yellow crystalline precipitate of an ammonium salt and complex arsenomolybdic acid $H_7[As(Mo_2O_7)_6]$.

The reaction may be represented by the equation**

$$AsO_4^{---} + 3NH_4^+ + 12MoO_4^{--} + 24H^+ = \downarrow (NH_4)_3H_4[As(Mo_2O_7)_6] + 10H_2O$$

The precipitate is readily soluble in excess arsenate to form a complex anion. Therefore *a relatively large amount of reagent must be added for this reaction.*

To carry out the test, add about 5 ml of ammonium molybdate solution to 1 ml of the arsenate solution, followed by a small amount of solid NH_4NO_3 (which raises the sensitivity of the reaction by the action of the common NH_4^+ ion) and heat for several minutes.

The precipitate is insoluble in nitric acid, but dissolves readily in caustic alkalies and in ammonia The PO_4^{---} ion forms a precipitate

---

* A mixture of $MgCl_2$, NH_4Cl and NH_4OH (see Appendix, Table 1, p. 530).

** This equation is somewhat simplified. In reality, the precipitate also contains $4H_2O$ molecules, forming H_3O^+ ions with H^+. Therefore the complete formula of ammonium arsenomolybdate is $(NH_4)_3(H_3O)_4[As(Mo_2O_7)_6]$.

of analogous composition, $(NH_4)_3H_4[P(Mo_2O_7)_6]$, but this is formed even in the cold whereas to precipitate $(NH_4)_3H_4[As(Mo_2O_7)_6]$, the solution must be heated almost to boiling.

5. Reduction of As^{III} and As^{V} Compounds to AsH_3. For detection of small amounts of arsenic in various substances, use is very often made of the highly sensitive reaction of As^{III} and As^{V} compounds to gaseous arsine.

The formation of AsH_3 can be detected by various methods; the most convenient is blackening of paper moistened with $AgNO_3$ solution. The paper is blackened as the result of reduction of Ag^+ ions by arsine to metallic silver.

a. Reduction in acid solution by N. A. Tananaev's method is performed as follows. Put 1-2 ml of HCl in a crucible, stand the crucible on a piece of filter paper, and moisten the paper (to one side of the crucible) with a drop of $AgNO_3$ solution. Next put a piece of metallic magnesium (or zinc*) into the crucible, and immediately cover the crucible and the moist spot by a small funnel with its tube sealed or firmly plugged with cotton wool. Examine the paper after a few minutes; if it is not blackened, the reagents are pure and can be used for the arsenic test.

To test for arsenic, repeat the above procedure, putting into the crucible *a very small amount* (2-3 drops) of the unknown solution** together with HCl and magnesium (or zinc). In the presence of arsenic the paper blackens rapidly owing to reduction of Ag^+ ions to the metal by the AsH_3 evolved.

The equations for the reactions are:
in the crucible

$$AsO_3^{---} + 9H^+ + 3Mg = AsH_3\uparrow + 3Mg^{++} + 3H_2O$$

on paper

$$AsH_3 + 6Ag^+ + 3H_2O = \downarrow 6Ag + H_3AsO_3 + 6H^+$$

Under these conditions, antimony forms gaseous stibine, SbH_3, which also blackens paper moistened with $AgNO_3$. In addition, sulphides must be absent, because the hydrogen sulphide evolved by the action of HCl on them would also blacken the paper by forming Ag_2S.

b. Reduction in alkaline solution is performed similarly, but concentrated (20-25%) NaOH solution is used instead of HCl, and aluminium powder or zinc dust*** is taken instead of magnesium. With

---

* If Zn is used, concentrated HCl should be taken.

** Remember that AsH_3, like all other arsenic compounds, is *very poisonous*.

*** In the latter case the solution in the crucible should be warmed. Of course, preliminary testing for purity of the reagents is essential.

zinc dust the reaction is

$$AsO_3^{---} + 3Zn + 3OH^- = AsH_3\uparrow + 3ZnO_2^{--}$$

In alkaline solution only AsO_3^{---} ions and not AsO_4^{---} ions are reduced to AsH_3. Therefore AsO_4^{---} ions must first be reduced to AsO_3^{---} by the action of KI in the presence of H_2SO_4. The iodine liberated in the reaction is removed by evaporation of the solution to dryness (or until SO_3 fumes appear); the residue is then treated with excess alkali and aluminium or zinc dust as described above. Antimony is not reduced by these metals in alkaline solutions and does not interfere.

6. **Reduction of As^{III} and As^{V} to free arsenic** can be effected by the action of a saturated solution of $SnCl_2$ in concentrated HCl:

$$2As^{+++} + 3Sn^{++} = \downarrow 2As + 3Sn^{++++}$$

This reaction can be used for detecting arsenic in the presence of other cations by the following procedure. Put a few drops of the filtrate from the separation of the silver subgroup by the action of HCl into a crucible, and add small amounts of NH_4OH, H_2O_2, and $MgCl_2$ solutions. Hydrogen peroxide oxidizes trivalent arsenic compounds to AsO_4^{---}, which forms a precipitate of $MgNH_4AsO_4$ with ammonia and the magnesium salt. Evaporate the solution slowly to dryness and then heat strongly to volatilize any $HgCl_2$ which may be present (*in the fume cupboard*), as it would interfere. $MgNH_4AsO_4$ is converted on heating into the non-volatile salt $Mg_2As_2O_7$ (magnesium pyroarsenate), which remains in the crucible. Cool and treat the dry residue with a few drops of a saturated $SnCl_2$ solution in concentrated HCl, warming gently. In the presence of arsenic the solution turns brown, or black elemental arsenic is precipitated.

A solution of $SnCl_2$ in concentrated hydrochloric acid must be used as the reagent, because only As^{+++++} and As^{+++} cations are reduced to As, and these cations are formed in sufficient concentration only in strongly acid solutions (p. 386).

7. **Microcrystalloscopic Tests.** (a) The above reaction in which $MgNH_4AsO_4 \cdot 6H_2O$ crystals are formed is suitable for use as a microcrystalloscopic test for AsO_4^{---}. With the aid of a pointed glass rod join a drop of arsenate solution on a glass slide with a drop of magnesia mixture and examine the resultant crystals under the microscope. They are of the same form as $MgNH_4PO_4 \cdot 6H_2O$ crystals (see Figs. 12 and 13).

The test detects 0.05 μg As. The dilution limit is 1:20,000.

The AsO_3^{---} ion can form similar crystals if it is present at concentrations above 0.5-1%.

(b) Put a few small crystals of calcium acetate, $(CH_3COO)_2Ca$, into a drop of ammoniacal arsenate solution and cover with a cover slip (to protect from atmospheric CO_2). An amorphous precipitate

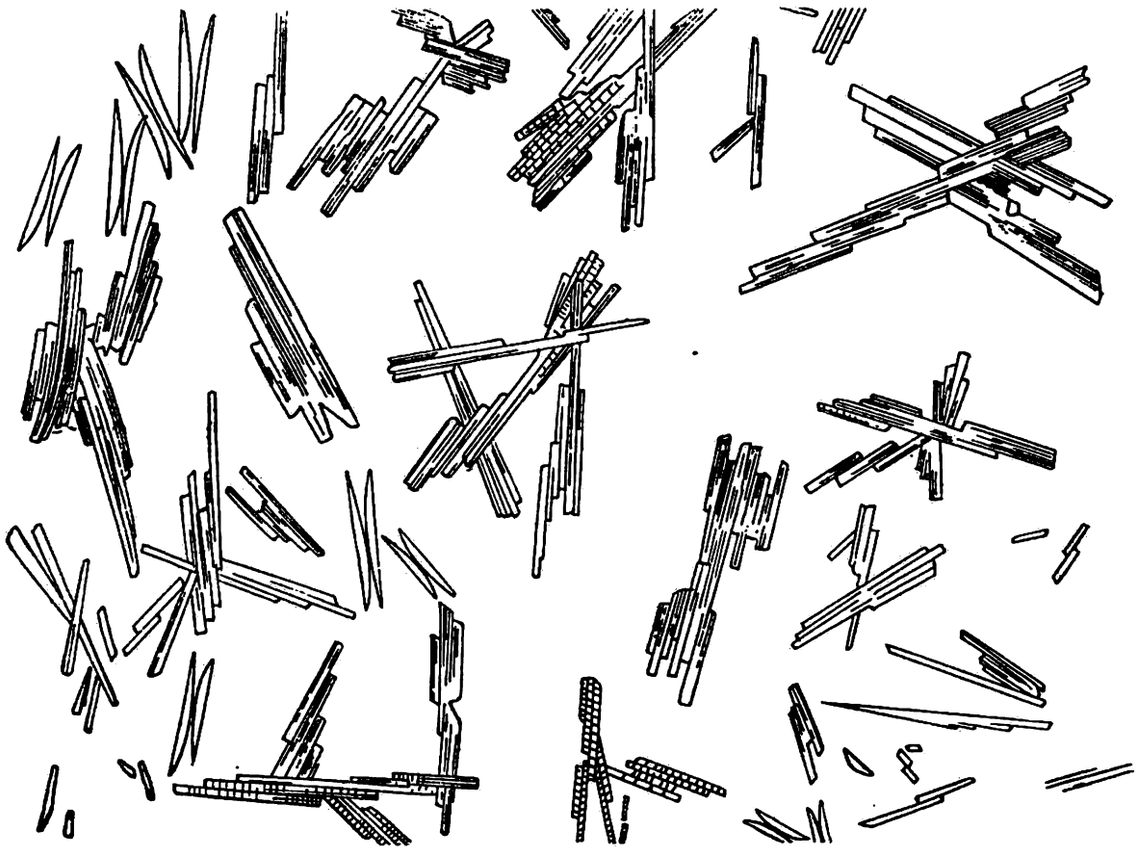


Fig. 40. Crystals of $CaNH_4AsO_4 \cdot 6H_2O$

is first formed, and this rapidly forms crystals of $CaNH_4AsO_4 \cdot 6H_2O$ (Fig. 40). The detectable minimum is 0.035 μg As. The dilution limit is 1:30,000.

77. Reactions of Antimony Ions

Antimony, like arsenic, forms two series of compounds; it is trivalent in one and quinquevalent in the other.

Solutions of antimony salts are colourless.

Reactions of antimony (III) ions

1. Action of Water (Hydrolysis). Dilute a solution of an antimonous salt with a large amount of water. A white precipitate of the salt SbOCl is formed:

$$[SbCl_6]^{---} + H_2O \rightleftarrows SbOCl + 5Cl^- + 2H^+$$

The reaction is analogous to the corresponding reaction of the Bi^{+++} ion.

The SbOCl precipitate dissolves on heating with excess HCl. In distinction from BiOCl, it also dissolves in tartaric acid to form the corresponding basic salt*:

$$SbOCl + H_2C_4H_4O_6 = SbOHC_4H_4O_6 + HCl$$

2. Caustic alkalies and ammonia give a white precipitate of metaantimonous acid:

$$[SbCl_6]^{---} + 3OH^- = \downarrow HSbO_2 + 6Cl^- + H_2O$$

Divide the precipitate into two portions; treat one with a strong acid and the other with a strong alkali. The precipitate dissolves in both cases. The reactions are:

$$HSbO_2 + 6H^+ + 6Cl^- = H_3[SbCl_6] + 2H_2O$$

$$HSbO_2 + NaOH = NaSbO_2 + H_2O$$

3. Sodium thiosulphate, $Na_2S_2O_3$, forms a white precipitate of antimony sulphoxide, Sb_2OS_2, when heated with antimonous salts. A large excess of acid, which decomposes the reagent with formation of SO_2 and sulphur, interferes.

4. Reduction of Sb^{+++} to metallic antimony. *a. Reduction by tin.* Put a drop of an antimonous salt solution on a piece of tin foil and leave to stand.

A black spot of metallic antimony is formed:

$$2[SbCl_6]^{---} + 3Sn = \downarrow 2Sb + 3Sn^{++} + 12Cl^-$$

The spot does not disappear when treated with a drop of freshly prepared NaBrO solution** (distinction from arsenic).

Before carrying out this test, wash off the acid solution remaining on the tin surface, because in the presence of acid the antimony spot may also disappear. It is evident that tin ions cannot interfere with detection of antimony by this test.

b. Reduction by zinc. Put 1-2 drops of a solution of an antimonous salt on platinum foil, and dip a piece of zinc into it so that the zinc and platinum touch each other. This forms a voltaic couple with Zn as the negative and Pt as the positive pole. The platinum gains electrons lost by zinc and transfers them to antimony ions, which are reduced to the metal. A black spot of metallic antimony appears

---

* The univalent group —Sb=O present in basic antimony salts is known as the antimonyl group. Therefore SbOCl can be called antimonyl chloride, $SbOHC_4H_4O_6$ is antimonyl hydrogen tartrate, etc.

** Prepared by addition of 2 *N* NaOH solution drop by drop to 2-3 drops of saturated bromine water until colourless (or pale yellow). The equation is

$$2NaOH + Br_2 = NaBrO + NaBr + H_2O$$

on the platinum foil. In contrast to tin, antimony is insoluble in HCl but dissolves in HNO_3.

Other metals apart from zinc which are to the left of Sb in the potential series (Mg, Fe, etc.) reduce trivalent antimony compounds to the metal.

5. Reaction with Methyl Violet. Add 3 ml of concentrated HCl (sp. gr. 1.19) and 1 ml of 1*N* KNO_2 or $NaNO_2$ solution to 1 ml of the solution to be tested for Sb^{III}. This oxidizes Sb^{III} to $[SbCl_6]^-$ anions,* which contain Sb^V. Leave the contents of the test tube to stand for at least 1 minute (to complete the reaction) and then add 1 ml of saturated urea solution, $CO(NH_2)_2$, to decompose excess nitrite. Dilute the solution to 3 ml with water, add 3-4 drops of 0.06 methyl violet solution** and shake the test tube.

In the presence of Sb a fine suspension is formed, consisting of crystals of a salt formed by the organic cation of the dye with the $[SbCl_6]^-$ anion, having a violet colour by transmitted light. In the absence of Sb the colour of the solution is yellow-green.

The test detects 0.5 μg Sb. Antimony can be detected by this test in the presence of Sn, Fe, Cu, Zn, and many other elements, which may be present in amounts more than 1,000 times the antimony content.

The organic dye rhodamine B***, which gives a blue or violet colour with antimony, reacts similarly. In the absence of Sb the colour is pink. The test is performed as described above, but there is no need to add urea.

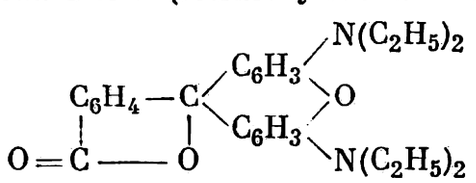
6. Phosphomolybdic Acid**, $H_7[P(Mo_2O_7)_6]$.** In our study of the reactions of the AsO_4^{---} ion we met a salt of the complex arsenomolybdic acid, $H_7[As(Mo_2O_7)_6]$. The PO_4^{---} ion forms phosphomolybdic acid $H_7[P(Mo_2O_7)_6]$, analogous in composition and structure. The sexivalent molybdenum contained in this compound has, as

---

* As it is not always possible to convert compounds of Sb^V into $[SbCl_6]^-$ by direct action of HCl, they must first be reduced to Sb^{III} by means of $SnCl_2$. The test is then performed as described, but a larger amount of nitrite must be taken (to oxidize excess $SnCl_2$).

** See footnote on p. 289.

*** The formula of rhodamine B (tetraethylrhodamine) is



The composition of the compound formed in this test is unknown.

**** Phosphomolybdic acid can be prepared by boiling its ammonium salt with aqua regia. After the salt has completely dissolved, the solution is evaporated to dryness; the dry residue is dissolved in water, recrystallized twice (from water), and kept in an orange glass bottle.

is sometimes the case in complex compounds, high reactivity; it can be reduced to a substance known as molybdenum blue (a mixture of various molybdenum compounds in a low state of oxidation) by reducing agents which do not react with molybdic acid and normal molybdates (these include Sb^{III}). The following spot test for Sb^{III} depends on this.

Put a drop of the solution to be tested for Sb^{III} on a piece of filter paper soaked in 5% phosphomolybdic acid solution and dried. Hold the paper for a few minutes in water vapour. A blue colour appears in the presence of Sb^{III}.

The reaction detects 0.2 μg Sb. The dilution limit is 1:250,000.

A similar colour is produced by Sn^{++} ions, which must be absent for this test. Stannic salts do not interfere.

7. Potassium mercuric iodide, $K_2[HgI_4]$, is reduced by Sb^{III} salts in the presence of alkali to metallic mercury, which forms a black precipitate. Salts of Sb^{III} give a similar reaction with $Hg(CN)_2$ solution; Sb^{V} does not give these reactions. Stannous ions react similarly to Sb^{III} and must be absent from the solution.

8. Hydroxyquinoline, C_9H_7ON, in the presence of potassium iodide in strongly acidic solution ($[H^+] = 6\text{-}7\ N$), forms a yellow precipitate which probably consists of a compound of hydroxyquinoline and the complex compound $HSbI_4$, with the composition $C_9H_7ON \cdot HSbI_4$ (compare the analogous reaction of Bi^{+++}, Sec. 72, 9). Tin and arsenic ions do not interfere, but cations of other groups should be absent. The test can therefore be used only in systematic analysis, after separation of Group V from Group IV.

In the acid method for separating Group V cations (see p. 404) a solution is obtained which may contain 6 *N* hydrochloric acid and $[SnCl_6]^{--}$ and $[SbCl_6]^{---}$ ions. To detect antimony in the solution, rinse out a test tube with 6 *N* HCl solution (to remove water), put in 2-3 ml of the unknown solution, and add 1-2 ml of the reagent (mixture of hydroxyquinoline and KI, see p. 536). In the presence of antimony a yellow precipitate forms immediately at the boundary between the solutions. It dissolves on heating and reappears on cooling. It also dissolves when the solution is diluted with water. The detectable minimum is 2 μg Sb.

9. Microcrystalloscopic Test. When a grain of KI and a grain of RbCl (or CsCl) are put successively into a drop of a weakly acidic solution of an antimony (III) salt, red hexagonal crystals are formed, of exactly the same form as in the case of Bi^{+++} (see Fig. 39, p. 365). The probable composition of the precipitate is $Rb_2[SbI_5] \cdot 2.5H_2O$ (or $Cs_2[SbI_5] \cdot 2.5H_2O$). The test can detect 0.1 μg Sb. The dilution limit is 1:10,000. In the presence of Sn^{IV} colourless crystals of $Rb_2[SnCl_6]$ or $Cs_2[SnCl_6]$ are formed (p. 401), but they do not interfere with detection of the red crystals of the complex antimony salt.

Reactions of antimony (V) ions

1. **Action of Water.** When a solution of an Sb^V salt is diluted with water, a white precipitate of the basic salt SbO_2Cl is formed:

$$[SbCl_6]^- + 2H_2O = \downarrow SbO_2Cl + 5Cl^- + 4H^+$$

The precipitate dissolves on heating with excess HCl.

2. **Caustic alkalies and ammonia solution** give a white precipitate of metaantimonic acid:

$$[SbCl_6]^- + 5OH^- = \downarrow HSbO_3 + 6Cl^- + 2H_2O$$

3. **Metallic Sn, Zn, Mg, Al and Fe** have the same effect on Sb^V salts as on Sb^{III} salts.

78. Reactions of Tin Ions

Tin forms two series of compounds: stannous salts, in which it is bivalent, and stannic salts in which it is quadrivalent. Solutions of tin salts are colourless.

Reactions of stannous ions

1. **Caustic alkalies, KOH and NaOH,** give a white precipitate of $Sn(OH)_2$ with Sn^{++}:

$$Sn^{++} + 2OH^- = \downarrow Sn(OH)_2 \text{ (or } H_2SnO_2)$$

The precipitate is soluble in both acids and alkalies (test this). When dissolved in alkalies, it forms stannites (SnO_2^{--} ions):

$$H_2SnO_2 + 2OH^- = SnO_2^{--} + 2H_2O$$

Ammonia solution gives a precipitate of $Sn(OH)_2$ which does not dissolve in excess NH_4OH.

2. **Reduction of Ammonium Phosphomolybdate.** Add 3-4 ml of ammonium molybdate solution to 1 ml of Na_2HPO_4 solution and warm slightly. On cooling, dilute the contents of the test tube together with the precipitated $(NH_4)_3H_4[P(Mo_2O_7)_6]$ by 10 ml of water and then add, drop by drop, the solution to be tested for Sn^{++}. A blue colour indicates the presence of Sn^{++}. The course of the reaction is explained as follows. The reaction between Na_2HPO_4 and ammonium molybdate is similar to that used for detection of AsO_4^{---} ions (p. 390):

$$PO_4^{---} + 3NH_4^+ + 12MoO_4^{--} + 24H^+ = \downarrow (NH_4)_3H_4[P(Mo_2O_7)_6] + 10H_2O$$

The sexivalent molybdenum contained in the sparingly soluble complex salt formed is an oxidizing agent and can oxidize Sn^{++} ions to Sn^{++++}. It is itself reduced to the substance known as "molybdenum blue", a blue mixture of molybdenum compounds of various valencies.

The Sb^{+++} ion cannot reduce $(NH_4)_3H_4[P(Mo_2O_7)_6]$ and therefore does not interfere. On the other hand, free phosphomolybdic acid is also reduced by Sb^{+++} ions.

When this test is used for detection of tin in analysis, it must be remembered that tin is present in the solution in the form of $[SnCl_6]^{--}$ anions. The latter must therefore be reduced to Sn^{++} by means of magnesium metal in the presence of HCl.

3. Metallic zinc reduces stannous and stannic ions to the free metal, deposited in the form of a grey spongy layer. In distinction from antimony, tin is soluble in HCl. Therefore the solution should not be too acid for this test.

4. Reduction Reactions with the Sn^{++} Ion. The standard oxidation potential of the Sn^{++++}/Sn^{++} couple is $+0.15$ V. Therefore the Sn^{++} ion is a fairly strong reducing agent, capable of reducing many oxidizing agents with higher oxidation potentials. Some examples of these reduction reactions are examined below.

a. Reduction of Hg^{++}. Add $HgCl_2$ solution drop by drop to $SnCl_2$ solution. A white precipitate of Hg_2Cl_2 is formed; in the presence of excess Sn^{++} it gradually turns grey owing to further reduction to metallic mercury:

$$2HgCl_2 + SnCl_2 = \downarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

This reaction was described earlier (p. 355) as a test for the Hg^{++} ion, but it is no less important as a test for Sn^{++}.

b. Reduction of Bi^{+++}. Remember the reaction between stannite solution and bismuth hydroxide, used for detection of Bi^{+++}:

$$2Bi(OH)_3 + 3SnO_2^{--} = \downarrow 2Bi + 3SnO_3^{--} + 3H_2O$$

The procedure is described on p. 363.

c. Reduction of Fe^{+++} *to* Fe^{++}. Add 2 *N* HCl and $K_3[Fe(CN)_6]$ solution to a solution of a ferric salt. Add a solution of a stannous salt to the mixture. A dark blue precipitate of Turnbull's blue is immediately formed. The course of the reaction is clear from the following equations:

$$2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++}$$

$$3Fe^{++} + 2[Fe(CN)_6]^{---} = \downarrow Fe_3[Fe(CN)_6]_2$$

d. Reduction of picric acid, $C_6H_2(NO_2)_3OH$. The reduction of picric acid to picramic acid, $C_6H_2(NO_2)_2(NH_2)OH$ is very characteristic for the Sn^{++} ion. It is most conveniently performed as a spot test on a strip of newspaper. A drop of aqueous picric acid is put on the newspaper, followed by a drop of the unknown solution. The solutions are absorbed better if the paper is warmed slightly. In the presence of Sn^{++} the spot acquires an intense orange colour owing to formation of picramic acid.

The test can also be performed in alkaline solution in a test tube. Picric acid (1 ml) is added to 5 ml of the unknown solution, followed by NH_4OH added drop by drop until $Sn(OH)_2$ is precipitated, and the liquid is heated. The picramic acid gives a red colour in the solution and precipitate.

Only silver and mercury ions, which are reduced to the metals, interfere with the test; their black colour masks the red colour due to the presence of Sn^{++}.

If tin is present in the form of Sn^{++++} ions, they are first reduced to Sn^{++} by means of metallic aluminium or magnesium. The reduction is effected in the presence of HCl on heating and standing for a few minutes.

Reactions of stannic ions

1. Caustic alkalies and ammonia form a white gelatinous precipitate of orthostannic acid, $Sn(OH)_4$ or H_4SnO_4, e.g.:

$$[SnCl_6]^{--} + 4OH^- = \downarrow H_4SnO_4 + 6Cl^-$$

The precipitate dissolves in alkalies to form stannates, e.g.:*

$$H_4SnO_4 + 2NaOH = Na_2SnO_3 + 3H_2O$$

It is also soluble in concentrated HCl with formation of the complex chlorostannic acid:

$$Sn(OH)_4 + 6HCl = H_2[SnCl_6] + 4H_2O$$

2. Reduction of Sn^{IV} to Sn^{II}. In the course of analysis, when the sulphide SnS_2 is dissolved in HCl, tin goes into solution in the form of complex $[SnCl_6]^{--}$ ions. These ions contain Sn^{IV}, whereas tin is usually detected by the reducing properties of Sn^{++} ions. It is therefore necessary to reduce $[SnCl_6]^{--}$ ions to Sn^{++}. The reduc-

* The formula given for the stannate is simplified. In reality, the structure of the stannate corresponds to the complex hexahydroxystannic acid, $H_2[Sn(OH)_6]$, known as α-stannic acid. Another form is known, β-stannic acid, which differs from α-stannic acid by being insoluble in acids; its formula is $[H_2SnO_3]_5$. It is formed by the action of concentrated HNO_3 on metallic tin.

tion can be effected by magnesium, iron, or other metals; e.g.:

$$Mg + [SnCl_6]^{--} = Mg^{++} + Sn^{++} + 6Cl^-$$
$$Fe + [SnCl_6]^{--} = Fe^{++} + Sn^{++} + 6Cl^-$$

Metallic iron reduces quadrivalent tin only as far as Sn^{++}, but not to the metal. On the other hand, when magnesium is used for the reduction and insufficient acid is present, a grey precipitate of metallic tin may be formed. On addition of a few drops of concentrated HCl the tin dissolves to form Sn^{++} ions:

$$Sn + 2H^+ = Sn^{++} + H_2 \uparrow$$

3. Microcrystalloscopic Test. Tin can be detected without the need to reduce Sn^{IV} to Sn^{II} by means of a microcrystalloscopic test for $[SnCl_6]^{--}$. Put a small crystal of RbCl or CsCl into a drop

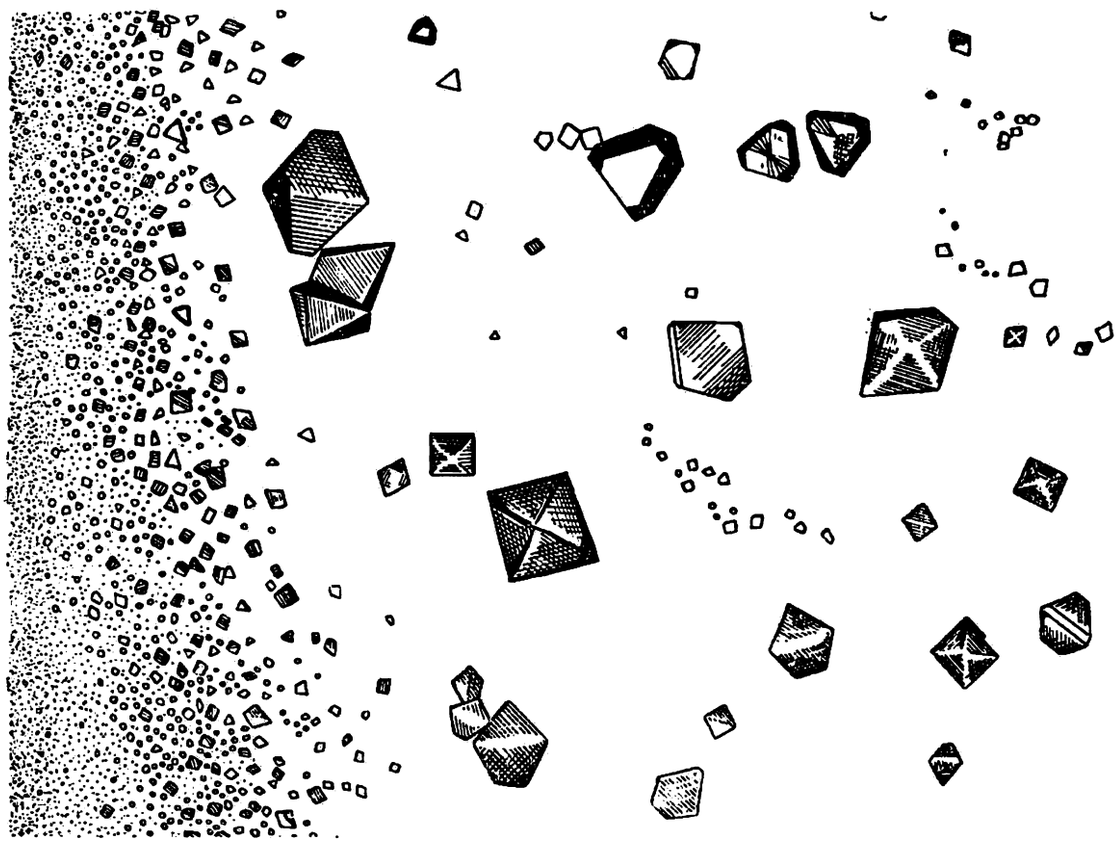


Fig. 41. Crystals of $Rb_2[SnCl_6]$

of the solution of the Sn^{IV} salt in hydrochloric acid, and leave to stand. In the presence of tin the crystal becomes surrounded by a white cloudy precipitate of sparingly soluble $Rb_2[SnCl_6]$ or $Cs_2[SnCl_6]$. Under the microscope, the crystals of these salts appear as small octahedra (Fig. 41). The large crystals usually form at the

edges of the precipitate. Increase of the HCl concentration lowers the crystallization rate and thus favours the formation of crystals.

Very similar crystals are formed by ammonium ions* with $[SnCl_6]^{--}$. The $(NH_4)_2[SnCl_6]$ crystals are usually larger and better formed than $Rb_2[SnCl_6]$ crystals. The test is carried out on a glass slide. A drop of 1 *N* ammonia solution is added to a drop of a solution of a stannic salt in hydrochloric acid. If turbidity due to hydroxides appears, a drop of 2 *N* HCl is added, the solution is warmed slightly until a border forms around its edges, and the liquid is left to cool. After 2 minutes the $(NH_4)_2[SnCl_6]$ crystals are examined under the microscope. In most cases they are relatively large colourless octahedra (see Fig. 41). None of the other cations usually met in analysis, including titanium, vanadium, molybdenum and tungsten, interferes with the test. Of course, cations which are precipitated by Cl^- ions should first be removed. Moreover, before the test is carried out stannous tin must be oxidized to the stannic form by the action of H_2O_2 in the presence of HCl. Under such conditions the test is suitable for fractional detection of tin in a separate portion of the unknown solution. The detectable minimum is 0.05 μg and the dilution limit is 1:20,000.

Antimony does not interfere even at a concentration ratio [Sb] : [Sn] = 100 : 1.

4. Reduction of Sn^{IV} and Sn^{II} to SnH_4. The reduction of tin salts to SnH_4 by means of zinc and concentrated HCl is a highly characteristic reaction. The formation of this compound is easily detected, because it confers a very characteristic cornflower-blue colour to the non-luminous burner flame.

Put a small amount of concentrated HCl in a porcelain basin, add the solution to be tested for tin (for example, $SnCl_2$ or $SnCl_4$), and put in a few small pieces of metallic zinc.** Stir the liquid in the basin by means of a test tube half filled with water (to prevent subsequent cracking). Now put the test tube in the burner flame and observe the blue colour which appears after some time near the surface of the tube.

79. Analysis of Mixtures of Group V Ions

The effects of the most important reagents on the ions formed by elements of analytical Group V are compared in Table 25***.

---

* The reaction of $(NH_4)_2[SnCl_6]$ formation was first proposed by R. K. Korabel'nik.

** The zinc must be free from tin; confirm this by a blank experiment.

*** Because of their close connection with the reactions of Hg_2^{++}, the reactionsof the Hg^{++} cation were given earlier, in Table 22 (p. 369).

Reagents	Ions	
	AsO_3^{---}	AsO_4^{---}
H_2S in presence of HCl	Yellow precipitate As_2S_3	Yellow precipitate As_2S_3 (or As_2S_5)
Action of Na_2S and $(NH_4)_2S_2$* on sulphides	Dissolves to form thiosalt	Dissolves to form thiosalt
Action of HCl on sulphides	Insoluble	Insoluble
Action of $(NH_4)_2CO_3$ on sulphides	Dissolves	Dissolves
H_2O	—	—
Caustic alkalies and NH_4OH	—	—
Metallic Fe in presence of HCl	—	—
Bismuth (III) salts in alkaline solution	—	—
$HgCl_2$	—	—
$MgCl_2$ in presence of NH_4OH and NH_4Cl	—	White crystalline precipitate $MgNH_4AsO_4$
$(NH_4)_2MoO_4$ in presence of HNO_3	—	Yellow precipitate $(NH_4)_3H_4[As(Mo_2O_7)_6]$
$AgNO_3$	Yellow precipitate Ag_3AsO_3	Chocolate-brown ppt. Ag_3AsO_4
Oxidizing agents	AsO_4^{---}	—

* Na_2S dissolves sulphides without changing the valencies of the elements. On the other hand, $(NH_4)_2S_2$ oxidizes them to form thiosalts corresponding to the highest valencies of As, Sb, and Sn, namely: $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ and $(NH_4)_2SnS_3$.

** The sulphides dissolve in $(NH_4)_2S_2$ because SnS is oxidized to SnS_2.

*** Reaction proceeds in alkaline solution.

Table 25

and Tin Ions

Ions			
$[SbCl_6]^{---}$	$[SbCl_6]^{-}$	Sn^{++}	$[SnCl_6]^{--}$
Orange-red precipitate Sb_2S_3	Orange-red precipitate Sb_2S_5	Brown precipitate SnS	Yellow precipitate SnS_2
Dissolves to form thiosalt	Dissolves to form thiosalt	Insoluble in Na_2S **	Dissolves to form thiosalt
Dissolves	Dissolves	Dissolves	Dissolves
Insoluble	Insoluble	Insoluble	Insoluble
White ppt. SbOCl	White ppt. SbO_2Cl	White precipitate of basic salts	White precipitate of basic salts
White precipitate $HSbO_2$	White precipitate $HSbO_3$	White precipitate $Sn(OH)_2$	White precipitate H_4SnO_4
Black precipitate Sb	Black precipitate Sb	—	Reduced to Sn^{++}
—	—	Black precipitate Bi	—
—	—	White precipitate, turning grey $Hg_2Cl_2 \rightarrow Hg$	—
—	—	—	—
—	—	—	—
—	—	Black precipitate Ag ***	—
Sb^{V}	—	Sn^{IV}	—

We already know that in systematic analysis the acid filtrate obtained after separation of the silver subgroup by the action of HCl is saturated (at pH = 0.5) with hydrogen sulphide, which precipitates the sulphides of the copper subgroup and of Group V, while cations of Groups I-III remain in solution. The precipitate is treated with the Group V group reagent, Na_2S, which dissolves out this group in the form of thiosalts while sulphides of the copper subgroup remain in the precipitate. The thiosalts are then decomposed by acid, and Group V sulphides are again precipitated.

The precipitate can then be analyzed further by different methods.

a. The acid method is based on the different effects of concentrated HCl on the sulphides; the sulphides of antimony and tin are dissolved, while the sulphides of arsenic and mercury remain in the precipitate.

b. The alkali method depends on the fact that the sulphides of arsenic dissolve in $(NH_4)_2CO_3$ while the other Group V sulphides do not.

Both these methods are used in the description and analytical table given below (see Table 26, p. 409). The precipitated sulphides are first separated by means of HCl. Then, to separate arsenic from mercury, the residue containing As_2S_3 and HgS, not dissolved in HCl, is treated with $(NH_4)_2CO_3$, when arsenic is dissolved as $(NH_4)_3AsS_3$ and $(NH_4)_3AsO_3$ while HgS remains in the residue.

In earlier analyses we always attempted to determine the valency as well as the presence of ions in mixtures. In analysis of Group V it is difficult to determine the valencies of arsenic, antimony and tin, as they vary repeatedly during the analysis; in relation to arsenic ions this question is discussed in Chapter VIII.

ANALYSIS OF MIXTURES OF IONS OF GROUPS V-I

1. Preliminary Observations and Tests. (a) Note the colour of the solution and draw what inferences you can concerning the presence of coloured ions, such as Cu^{++}, Cr^{+++}, Co^{++} or Ni^{++}.

(b) Determine the solution pH without preliminary neutralization and, if necessary, after neutralization. A strongly acid reaction may be due to the presence of antimony and tin salts, which are highly hydrolyzed in aqueous solutions, as well as to Fe^{+++}, Bi^{+++} and mercury ions.

An alkaline reaction may be due to the presence of AsO_3^{---} and AsO_4^{---} anions, and also to SnO_2^{--}, SnO_3^{--}, SbO_3^{---} and SbO_4^{---}. In addition, alkaline solutions may contain thiosalts of Group V elements, i.e., the anions AsS_3^{---}, AsS_4^{---}, SbS_3^{---}, SbS_4^{---} and SnS_3^{--}.

(c) Test for Fe^{+++}, Fe^{++} and NH_4^+ in separate portions of the solution by the usual tests.

2. Separation of Cations of the First Subgroup of Group IV. Start the systematic analysis (regardless of the presence of any precipitate in the unknown solution) by precipitating the cations of the first subgroup of Group IV by HCl (p. 347, 2).

The precipitate may contain* AgCl, Hg_2Cl_2, $PbCl_2$, $PbSO_4$, $BaSO_4$, $SrSO_4$, $CaSO_4$ and some antimony, tin and bismuth in the form of basic salts. Investigate it as described for analysis of Group IV cations (pp. 367, 370-372, 3-8).

The filtrate contains ions of Group V together with cations of the second subgroup of Group IV and Groups III, II and I. Investigate it as described below.

3. Oxidation of Sn^{II} to Sn^{IV}. As SnS_2 is the only sulphide of tin to form a thiosalt, bivalent tin must be oxidized to the quadrivalent state before precipitation by H_2S.

Add 3-4 drops of 3% hydrogen peroxide to the solution and heat for several minutes to decompose excess H_2O_2.

The subsequent procedure is described in 4.

4. Adjustment of Solution Acidity and Precipitation of Groups IV and V by Hydrogen Sulphide. Combine the solution obtained in the preceding operations with the filtrate obtained when the basic salts were dissolved in HCl during investigation of the precipitate of the first subgroup of Group IV (see p. 370, 7), and adjust the acidity to the level required** for precipitation by H_2S (pH = 0.5). First add 13 *N* NH_4OH until the solution is weakly alkaline (pH $\approx$ 9), destroy the excess by addition of 2 *N* HCl until slightly acid (pH = 3-5), and finally add more 2 *N* HCl in a volume equal to 1/5 of the total volume of the solution. Add two drops of NH_4I solution*** to the liquid (its HCl concentration is now about 0.3 *M*).

Ignore any iodides which may be precipitated**** and pass H_2S gas through the solution for 5-7 minutes. Keep the test tube in water heated to 70-80° C. Dilute the contents of the tube with an equal volume of cold distilled water and again pass H_2S for 2-3 minutes. Filter off the precipitate and test for complete precipitation by means of *freshly prepared* H_2S water. If the precipitation is incom-

---

* We are not considering the case when the precipitate may also contain β-stannic acid $(H_2SnO_3)_5$ or metaantimonic acid $HSbO_3$. The solution of these compounds is discussed on p. 497.

** It will be remembered that Group V ions are not precipitated by hydrogen sulphide in alkaline solutions (p. 384). The solution must also be acid to prevent precipitation of ZnS by the action of H_2S (p. 183). However, the acidity must not be too high, otherwise the precipitation of such cations as Cd^{++} and Sn^{++++} may be incomplete.

*** NH_4I is added to accelerate precipitation of As^V. An alcoholic solution of iodine may be used instead; hydrogen sulphide reduces I_2 to I^-.

**** Iodides are converted into the less soluble sulphides by the action of H_2S.

plete, dilute the solution again with water and pass H_2S. Continue this procedure until the precipitation is complete. The precipitate may contain CuS, CdS, Bi_2S_3, PbS (part) and Group V sulphides; wash it with water containing NH_4Cl and investigate as described in 5.

Investigate the filtrate as directed on p. 376, 14.

5. Separation of Groups IV and V. Treat the washed sulphide precipitate with alkaline Na_2S solution with gentle warming and stirring for 2-3 minutes. Group V sulphides dissolve to give the corresponding thiosalts while Group IV sulphides remain in the residue. Dilute with water and filter. Then treat the precipitate with sodium sulphide again.

Combine the filtrates from the two treatments and investigate according to 6.

The precipitate may contain CuS, CdS, Bi_2S_3 and PbS; wash it with water containing a small amount of NH_4Cl and investigate it either as described on pp. 372-373 or by the alkaline glycerol method (p. 376).

6. Decomposition of Thiosalts. The combined filtrate may contain AsS_3^{---}, SbS_4^{---}, SnS_3^{--} and HgS_2^{--} ions, together with excess Na_2S and NaOH. Add concentrated CH_3COOH drop by drop (with continuous stirring) to an acid reaction ($pH \ll 5$)*. Thiosalts are decomposed and the corresponding sulphides As_2S_3, Sb_2S_5, SnS_2 and HgS, together with sulphur formed from sodium sulphide**, are precipitated.

Heat the test tube with the precipitate for several minutes on a water bath, filter, and test for complete precipitation by adding CH_3COOH. When the precipitation is complete, discard the filtrate. Wash the precipitate with water containing NH_4Cl and investigate as indicated in 7.

7. Separation of As and Hg from Sb and Sn. Heat the precipitated sulphides for 3-5 minutes with concentrated (12 *N*) HCl and an equal volume of water. The sulphides of tin and antimony dissolve to form $[SbCl_6]^{---}$ and $[SnCl_6]^{--}$ ions***, while As_2S_3 and HgS, which are insoluble in HCl, remain in the residue together with sulphur*.

---

* Avoid a large excess of CH_3COOH.

** Sulphur is formed by the action of acetic acid on polysulphides (present in Na_2S solution owing to oxidation by atmospheric oxygen), for example:

$$Na_2S_2 + 2CH_3COOH = 2CH_3COONa + H_2S\uparrow + \downarrow S$$

The sulphur precipitate is milky white in appearance, whereas the Group V sulphides may be yellow (SnS_2 and As_2S_3), orange-red (Sb_2S_5) or black (HgS). Therefore if a white precipitate forms when the solution is acidified with CH_3COOH Group V must be absent.

*** It will be remembered that when Sb_2S_5 dissolves in HCl Sb^V is reduced to Sb^{III} (p. 387) and the complex acid $H_3[SbCl_6]$ is formed. Under the same conditions Sn^{IV} is not reduced, but forms the complex acid $H_2[SnCl_6]$ (p. 399).

Wash the precipitate with water containing KNO_3 and investigate according to 8. Investigate the filtrate as described in 11.

8. Separation of As from Hg. Add water and excess solid** $(NH_4)_2CO_3$ to the washed precipitate and warm *gently* with stirring for about 1 minute. As_2S_3 is dissolved to form $(NH_4)_3AsS_3$ and $(NH_4)_3AsO_3$, while HgS and S remain in the residue.

Filter, wash the precipitate with water containing NH_4Cl, and investigate it according to 10.

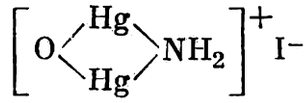
For investigation of the filtrate see 9.

9. Detection of As. (a) To a portion of the filtrate, containing $(NH_4)_3AsS_3$, $(NH_4)_3AsO_3$ and excess $(NH_4)_2CO_3$, *cautiously**** add 2 *N* HCl until acid. A yellow precipitate of As_2S_3 indicates the presence of As.

(b) Heat the rest of the filtrate for 1-2 minutes with a few drops of H_2O_2 solution. This oxidizes AsS_3^{---} and AsO_3^{---} ions to AsO_4^{---}.

To test for As, acidify the solution with HNO_3, add a small amount of solid NH_4NO_3, and treat with excess ammonium molybdate solution****. Heat for 5-10 minutes. A yellow crystalline precipitate of $(NH_4)_3H_4[As(Mo_2O_7)_6]$ confirms the presence of As. Alternatively, AsO_4^{---} can be detected in the alkaline solution after treatment with H_2O_2 by the reaction with magnesia mixture (p. 390, 3) or by the microcrystalloscopic test (p. 392, 7).

10. Detection of Hg^{++}. Treat the precipitate containing HgS and S for 2-3 minutes with a mixture of concentrated (12 *N*) HCl and KI solutions, heating and stirring. HgS dissolves to form complex $[HgI_4]^{--}$ ions. Filter off and discard the undissolved residue (S), heat to remove the H_2S formed during the reaction*****, and then add 1 drop of 2 *N* NH_4OH followed by excess of concentrated NaOH solution. A red-brown precipitate



indicates the presence of Hg^{++}.

---

* Small amounts (traces) of arsenic and mercury sulphides may, however, dissolve. It is therefore advisable to pass H_2S through the hot liquid for about 1 minute before filtration in order to reprecipitate them.

** The $(NH_4)_2CO_3$ solution, used for precipitation of Group II cations, cannot be used in this case because it contains NH_4OH and would therefore dissolve the sulphides of tin and antimony if these have not been completely dissolved in HCl. As a result, arsenic may be incorrectly reported as present.

*** If the HCl is added too rapidly, the CO_2 evolved may eject the liquid from the test tube.

**** NH_4NO_3 is added to lower the solubility of the precipitated $(NH_4)_3H_4[As(Mo_2O_7)_6]$. A large excess of ammonium molybdate solution must be added, otherwise a precipitate is not formed because of its solubility in excess arsenate.

***** If this is not done, HgS is formed instead of the required precipitate.

Note. The following is an alternative test for Hg^{++}. Heat the precipitate with a few drops of aqua regia. When the HgS has dissolved, filter off the sulphur and evaporate the filtrate very cautiously in a crucible to remove excess aqua regia (not to dryness, as otherwise the $HgCl_2$ formed during the reaction would volatilize). Dilute the solution with water and test a separate portion with $SnCl_2$. A white precipitate, turning grey in the presence of excess reagent ($Hg_2Cl_2 \rightarrow Hg$), indicates the presence of Hg^{++}.

11. Detection of Sn and Sb. Test for tin and antimony in the filtrate obtained in 7, containing $[SbCl_6]^{---}$ and $[SnCl_6]^{--}$ ions in excess HCl.

a. Detection of Sn. Add a drop of 2 *N* NH_4OH to a drop of the solution. If a precipitate is formed, acidify with a drop of 2 *N* HCl and warm gently until a border appears around the drop. On cooling, examine the crystals under the microscope. The formation of characteristic octahedral crystals of $(NH_4)_2[SnCl_6]$ (similar to those shown in Fig. 41, p. 400) indicates the presence of tin. The same test can be carried out with a drop of the original unknown solution, acidified with HCl, after removal of the precipitate of the first subgroup of Group IV and warming with a drop of H_2O_2 (to convert Sn^{++} ions into Sn^{++++}).

b. Detection of Sb. Put a drop of the solution on a piece of tin foil and leave to stand. If a black spot is formed, wash it thoroughly with water and treat with a drop of freshly prepared NaBrO solution (see p. 394). If the spot does not disappear, antimony is present*.

Alternative tests are the test with hydroxyquinoline and KI (Sec. 77, 8), or with methyl violet (Sec. 77, 5), or the spot test with phosphomolybdic acid (Sec. 77, 6). .

12. Reduction of Sn^{IV} to Sn^{II} and Confirmatory Tests for Sn^{++}. If the results of the test for formation of $(NH_4)_2[SnCl_6]$ crystals were inconclusive, confirmatory tests must be carried out. First, reduce Sn^{IV} to Sn^{II}. Add a piece of magnesium metal to the acid solution remaining from the tests in 11, and leave it to dissolve completely**. This reduces $[SnCl_6]^{--}$ to Sn^{++} or even to metallic tin, while $[SbCl_6]^{---}$ is reduced to antimony metal in the form of a black precipitate. When the magnesium has dissolved, add 1-2 drops of concentrated HCl and warm slightly to dissolve any tin metal formed. Filter off*** the Sb residue, and test the filtrate for Sn^{++}

---

* It will be remembered that arsenic also gives a black spot if it has been partially dissolved by the action of HCl on As_2S_3 (see 7). However, the arsenic spot disappears when treated with NaBrO while the Sb spot remains. In acid solution the Sb spot also disappears. Therefore the spot must be washed thoroughly with water to remove HCl.

** Add a few drops of HCl if necessary.

*** Alternatively, Sb can be dissolved by heating with HCl and H_2O_2 and the solution then tested for Sb.

Analysis of Mixtures of Groups V-I Cations

1. Preliminary tests—determine pH; test for NH_4^+, Fe^{++} and Fe^{+++}

2. Separate first subgroup of Group IV by HCl (in the cold)

Precipitate: AgCl, Hg_2Cl_2, $PbCl_2$, $PbSO_4$, $BaSO_4$, $SrSO_4$, $CaSO_4$ (and, partially, basicsalts of antimony, tin and bismuth). Investigate according to Table 23 on p. 375, 3-8

Filtrate: Cu^{++}, Cd^{++}, Pb^{++} (part), Bi^{+++}, As, Sb, and Sn ions, and cations of Groups III, II and I (HCl)

3. Oxidize Sn^{II} to Sn^{IV} by H_2O_2

4. Adjust acidity and precipitate Group V and the second subgroup of Group IV by hydrogen sulphide

Precipitate: CuS, CdS, PbS, Bi_2S_3, HgS, As_2S_3, Sb_2S_5, SnS_2 (S)

5. Separate ions of Groups IV and V by treatment of the solution with the Group V group reagent ($Na_2S + NaOH$)

Filtrate: cations of Groups III, II and I. Remove H_2S and concentrate the solution by evaporation. Examine for cations of Groups III-I (see Table 18 or 19, p. 309 or 314)

Precipitate: CuS, CdS, PbS, Bi_2S_3 (S). Dissolve in HNO_3, investigate by Table 23 (on p. 375) or by the alkaline glycerol method (p. 376)

Filtrate: AsS_3^{---}, SbS_4^{---}, SnS_3^{--}, HgS_2^{--} (Na_2S_1, NaOH)

6. Decompose thiosalts by CH_3COOH

Precipitate: As_2S_3, Sb_2S_5, SnS_2, HgS (S)

7. Separate As and Hg from Sb and Sn by means of HCl

Filtrate: CH_3COONa, CH_3COOH, H_2S. Not investigated

Precipitate: As_2S_3, HgS (S)

8. Separate As from Hg by means of $(NH_4)_2CO_3$

Filtrate: $[SbCl_6]^{---}$, $[SnCl_6]^{--}$, (HCl)

11. Test for $[SbCl_6]^{---}$ and $[SnCl_6]^{--}$

12. Reduce $[SnCl_6]^{--}$ and $[SbCl_6]^{---}$ by Mg

Residue: HgS, (S)

10. Dissolve in mixture of HCl and KI, remove H_2S, test for Hg^{++}

Filtrate: AsS_3^{---}, AsO_3^{---} $(NH_4)_2CO_3$

9. Test for As

Precipitate: metallic Sb, not investigated

Filtrate: Sn^{++} (Mg^{++}), test for Sn^{++}

(a) by the action of $HgCl_2$ (white precipitate of Hg_2Cl_2, turning grey in the presence of excess Sn^{++}) or (b) by the ammonium phosphomolybdate test (see p. 397) or with picric acid (p. 399).

13. Preparation of the Solution for Detection of Groups III, II and I. Evaporate the filtrate from the precipitation of Groups IV and V by hydrogen sulphide in a crucible to a small volume to remove excess H_2S and filter off the precipitated sulphur. Investigate the filtrate as described for analysis of Group III (pp. 302, 310 or 312).

80. Qualitative Analysis of Cations Without Use of Hydrogen Sulphide

The classical method for qualitative analysis of cations, described in this book, has the very serious disadvantage that hydrogen sulphide is used for group separation. This substance is very unpleasant to work with, harmful to health, and requires the use of a special hydrogen sulphide room with an efficient fume cupboard. Moreover, this method has a number of other disadvantages.

1. First, separation of analytical groups by the hydrogen sulphide method is not sufficiently sharp owing to coprecipitation and post-precipitation effects. For example, it was pointed out that when a precipitate of Group IV and V sulphides is left to stand in contact with the solution, post-precipitation of zinc sulphides occurs, as a result of which the Zn^{++} ion may be "missed". Similarly, Group III cations such as Ni^{++}, Co^{++}, etc., may be coprecipitated with cations of Groups IV and V.

2. Treatment with $(NH_4)_2S_2$ dissolves appreciable amounts of copper and mercury (II) sulphides in addition to the Group V sulphides. On the other hand, stannous sulphide is difficult to dissolve completely even by repeated treatment with $(NH_4)_2S_2$ solution.

3. The use of H_2S and $(NH_4)_2S$ solutions, which often contain SO_4^{--} ions (owing to oxidation of S^{--} ions by atmospheric oxygen), sometimes leads to "loss" of Group II cations, which are precipitated as sparingly soluble sulphates together with the sulphides of Groups III, IV and V. Group II cations can also be precipitated together with Group III because the ammonium sulphide and ammonia used for separating Group III cations often contain ammonium carbonate owing to absorption of CO_2 from the air.

4. Detection of Group I cations in the solution remaining after successive separation of all the other groups often leads to erroneous results because the concentration of these cations is very much lowered as the result of adsorption and other forms of coprecipitation, and the tests for them are of relatively low sensitivity. There-

fore, as already stated (p. 109) it is better to test for K^+ and Na^+ in separate portions of the unknown solution after precipitation of "heavy metals" by solutions of chemically pure sodium carbonate (in testing for K^+) or potassium carbonate (in testing for Na^+). Before testing for K^+ the NH_4^+ ion must be removed by evaporation and strong heating, or combined in the form of hexamethylenetetramine by the action of formaldehyde (p. 109).

5. Regulation of the acidity of the solution is very important in precipitation of sulphides. However, this operation is very difficult owing to precipitation of basic salts, which occurs long before the acid present in the solution has been completely neutralized. It is therefore necessary to add excess ammonia (until alkaline to litmus) and then to destroy the excess by addition of acid. As a result a large amount of ammonium salts accumulates in the solution and the salt effect is greatly intensified. Moreover, we must take into account the complex-forming action of Cl^- ions, which may lead to incomplete precipitation of Ag^+ in the form of AgCl (see p. 348) and of certain sulphides; for example, CdS is not precipitated from moderately acid solutions containing a large amount of NH_4Cl.

6. Dissolving Group IV sulphides in HNO_3 is also a somewhat inexact operation, because mercuric sulphide is generally partially dissolved together with Cu^{++}, Pb^{++}, Cd^{++} and Bi^{+++} ions, especially if Cl^- ions have not been completely washed out of the precipitate.

Other disadvantages of the hydrogen sulphide method could also be mentioned. Attempts have been and are still being made by various investigators to replace it by some other method, satisfactory from the chemical standpoint, for systematic analysis of cations without the use of H_2S.

In some of these methods the group separation is based, as in the classical method, on the properties of sulphides, but these are formed by some other reagents containing sulphur instead of H_2S. Such reagents include sodium thiosulphate $Na_2S_2O_3$, which precipitates many cations as sulphides in acid solution; ammonium polysulphide $(NH_4)_2S_2$; sodium sulphide Na_2S; ammonium thioacetate NH_4CH_3COS; ammonium dithiocarbonate $(NH_4)_2COS_2$, and other compounds. Since the sulphides precipitated by all these reagents have subsequently to be dissolved in acids, with evolution of H_2S, all these methods provide only a partial solution of the problem.

Other investigators break more decisively with the traditional method, as they consider correctly that the analyst can be released from the use of hydrogen sulphide only if the use of sulphides for separating groups or individual ions is abandoned entirely. In these methods the subdivision of cations into groups is based on the prop-

erties of other metallic compounds, such as hydroxides, phosphates, carbonates, etc., or of free metals.

For example, in the method proposed by I. S. Sakhiev the groups are separated as follows.

Group I: antimony and tin, precipitated as $HSbO_3$ and H_2SnO_3 by evaporation of the solution with HNO_3.

Group II: Ag^+, Hg_2^{++} and Pb^{++}, precipitated by hydrochloric acid.*

Group III: Fe^{+++}, Bi^{+++}, Cr^{+++}, Al^{+++}, Pb^{++} and Mn^{++}, precipitated by ammonia in the presence of ammonium chloride.

Group IV: Ba^{++}, Sr^{++}, Ca^{++}, precipitated by ammonium carbonate.

Group V: Cu^{++}, Cd^{++}, Zn^{++}, Ni^{++}, Co^{++}, Mg^{++}, precipitated by barium hydroxide.

Group VI: Na^+, K^+, NH_4^+—no group reagent.

Another example of a method without the use of H_2S is one based on differences between the properties of hydroxides of different metals, and on the solubilities of their chlorides and sulphates. The group separation by this method (the method of S. D. Beskov and O. A. Slizkovskaya) is effected as follows.

Group I: Ag^+, Hg_2^{++}, Pb^{++}; form sparingly soluble chlorides.

Group II: Ba^{++}, Sr^{++}, Ca^{++}; form sparingly soluble sulphates.

Group III: Al^{+++}, Cr^{+++}, Zn^{++}, As and Sn ions; form amphoteric hydroxides which remain in solution on addition of excess NaOH and H_2O_2 (cations of Groups IV and V are precipitated under these conditions).

Group IV: Fe^{+++}, Fe^{++}, Mn^{++}, Mg^{++}, Bi^{+++}, Sb^{+++}; form hydroxides which are not amphoteric and do not dissolve in excess ammonia.

Group V: Cu^{++}, Co^{++}, Ni^{++}, Cd^{++}, Hg^{++}; form hydroxides which dissolve in excess ammonia to form ammines.

Group VI: K^+, Na^+, NH_4^+.

The first step in analysis by this method is to precipitate Groups I and II by the action of HCl and H_2SO_4. After removal of these groups, NH_4^+, Na^+ and K^+ ions are detected by fractional tests in separate portions of the filtrate and the remaining solution is treated with excess NaOH and H_2O_2. Group III cations remain in solution while the hydroxides of Group IV and V cations are precipitated. The precipitate is treated with HNO_3; all the hydroxides dissolve except $HSbO_3$. This is filtered off, the acid in the filtrate is neutralized by Na_2CO_3, and excess ammonia is added. Group V cations remain in solution in the form of ammine complexes while Group IV hydroxides are precipitated.

---

* In this method Hg^{++} is reduced to Hg_2^{++} by the action of H_3PO_3; arsenic is volatilized in the form of the volatile chloride $AsCl_3$. Accordingly this classification does not include Hg^{++} ions or ions of tri- and quinquevalent arsenic

The method proposed by V. I. Petrashen should also be mentioned. The group separation in this method is based on different solubilities of phosphates in ammonia, acetic acid, and mineral acids. N. A. Tananaev proposed a method in which all the cations are divided into two large groups by treatment of the solution (of chlorides or nitrates) with metallic zinc powder. Some cations are reduced to the metals and are precipitated while others remain in solution.

Very many methods of qualitative analysis without the use of hydrogen sulphide have been described in detail in the specialized literature.

Despite the abundance of proposed methods, none has been widely adopted. The probable reason is that many of these methods suffer from at least as many disadvantages as the hydrogen sulphide method; the latter has the undoubted advantage that all its details have been thoroughly studied during the 120 years which have elapsed since it was first introduced. Moreover, the classical method of qualitative analysis is of great importance from the teaching standpoint, because it gives the best correlation between theory and analytical practice. The toxic effects of hydrogen sulphide are greatly reduced if the semimicro method is used. The adoption of the semimicro method is advisable for a number of other reasons (the analysis is more rapid, the consumption of reagents is reduced and the rarer and more costly reagents are therefore more accessible, the working place of the student is better organized and the work is therefore less tiring, etc.).

QUESTIONS AND PROBLEMS

1. State the properties of sulphides which distinguish Group V cations from (a) Group III cations; (b) Group IV cations.
2. What are thiosalts?
3. How are thiosalts formed? What is the action of acids on them? Write the equations for the reactions.
4. What group reagent is used for separating Group V from Group IV? Why is ammonium sulphide not used for this purpose?
5. Describe the effects of ammonium sulphide and polysulphide on SnS and As_2S_3.
6. What is the explanation of the acidic nature of the sulphides of Group V cations?
7. What is the action of H_2S on $NaAsO_2$? Explain why arsenic is precipitated by hydrogen sulphide only in acid solution.
8. Describe the action of hydrogen sulphide on solutions of arsenates (a) in moderately acid solutions on heating; (b) in strongly acid solutions in the cold.
9. How can the precipitation of arsenic (V) by hydrogen sulphide be accelerated?
10. Write the equations for the reactions taking place when (a) As_2S_3 and As_2S_5 are dissolved in NaOH and in $(NH_4)_2CO_3$; (b) the same sulphides are

dissolved in HNO_3 and in a mixture of NaOH and H_2O_2; (c) AsO_4^{---} ions are reduced to AsH_3 by metallic zinc in acid solution. How is the formation of AsH_3 detected?

11. What reactions distinguish arsenates from arsenites?

12. What methods are used for separating arsenic from antimony and tin?

13. What is the action of water on trivalent and quinquevalent antimony salts? Write the equations for the reactions.

14. What is the action of zinc and iron metals on antimony and tin salts?

15. Explain why metallic iron reduces Sn^{++++} ions to Sn^{++} but not to metallic tin.

16. Explain why Sn^{++} ions reduce Fe^{+++} to Fe^{++} but not to metallic iron.

17. Explain why Fe^{++} ions must be separated before testing for Sn^{++} ions by means of bismuth salts. How is the separation effected?

18. What will be found in the solution and in the precipitate if an excess of $(NH_4)_2S$ is added at once to a mixture of cations of all five groups, without previous treatment with HCl and H_2S?

CHAPTER VII

THE ELEMENTS TITANIUM, VANADIUM, MOLYBDENUM AND TUNGSTEN

81. General Characteristics

The elements Ti, V, Mo and W are usually classed with the "rare" elements. However, this is not an accurate description, as some of them occur quite widely in nature.* These elements are extensively used in the production of special steels and ferrous alloys.

These elements are in the first half of long periods 4, 5 and 6 of the Mendeleyev periodic system; as they belong to different groups, they differ quite considerably in chemical properties.

Titanium (Ti) belongs to Group IV of the periodic system. Its most important oxides are Ti_2O_3 and TiO_2. The former is a basic oxide and forms salts, such as $TiCl_3$, $Ti_2(SO_4)_3$, with acids; the salts are violet in colour. They are powerful reducing agents. The oxide TiO_2 is amphoteric. It gives rise, on the one hand, to salts such as $Ti(SO_4)_2$, $TiCl_4$, in which titanium is present as Ti^{++++} cations, and on the other, salts like Na_2TiO_3, K_2TiO_3, etc., in which titanium forms TiO_3^{--} anions. The acid H_2TiO_3 corresponding to these salts is known as metatitanic acid.

Vanadium (V) is an element in Group V of the periodic system. Its most important oxides are VO, V_2O_3, VO_2 and V_2O_5. The first two are basic. They form the salts VCl_2, $V_2(SO_4)_3$ and others, containing the cations V^{++} (violet) and V^{+++} (green). The oxide of quadrivalent vanadium, VO_2, is amphoteric. It gives rise to basic salts, such as $V_2O_2Cl_4$, etc., containing quadrivalent "divanadyl" ions $V_2O_2^{++++}$ (blue). It also reacts with alkalies to form salts known as vanadities, such as $Na_2V_4O_9$, etc.

The oxide V_2O_5 is an acidic anhydride. It gives rise to a series of acids: metavanadic HVO_3, orthovanadic H_3VO_4, and pyrovanadic $H_4V_2O_7$. These formulas show that the acids are analogous to the phosphoric acids in composition.

The salts of metavanadic acid (metavanadates) are the most important vanadium compounds. Polyvanadic acids are also known; they are formed by reactions of metavanadates with acid, e.g.,

$$6NaVO_3 + 6HCl = 6NaCl + H_4V_6O_{17} + H_2O$$

Molybdenum (Mo) belongs to Group VI of the periodic system. Its most important oxides have the formulas Mo_2O_3, MoO_2, Mo_2O_5 and MoO_3. They are all basic except the last. The highest oxide of molybdenum, MoO_3, is the anhydride of molybdic acid, H_2MoO_4. Its salts, the molybdates, such as $(NH_4)_2MoO_4$, are the commonest and most important compounds of this element.

---

* For example, titanium is one of the ten commonest elements. It is more abundant in the earth's crust than carbon, chlorine, phosphorus or sulphur. Vanadium is more abundant than copper, etc.

Tungsten (W) also belongs to Group VI of the periodic system. Its oxydes are WO_2, W_2O_5, WO_3 of which WO_3 is the most important; it gives rise to tungstic acid, H_2WO_4. Its salts, known as the tungstates, are the commonest compounds of tungsten. It should be noted that, in addition to normal tungstates and molybdates, sexivalent W and Mo also form numerous polytungstates and polymolybdates.

The ions corresponding to the highest valency states of these elements, namely: quadrivalent titanium (Ti^{++++}), quinquevalent vanadium (VO_3^-), and sexivalent molybdenum (MoO_4^{--}) and tungsten (WO_4^{--}), do not form a separate group and must be included in different analytical groups. The action of $(NH_4)_2S$ on these ions is the most important factor in deciding to which analytical groups they belong.

The action of $(NH_4)_2S$ precipitates Ti^{++++} ions in the form of $Ti(OH)_4$, for example*:

$$2(NH_4)_2S + 4H_2O \rightleftarrows 2H_2S + 4NH_4OH$$

$$Ti(SO_4)_2 + 4NH_4OH = Ti(OH)_4 + 2(NH_4)_2SO_4$$

$$Ti(SO_4)_2 + 2(NH_4)_2S + 4H_2O = \downarrow Ti(OH)_4 + 2(NH_4)_2SO_4 + 2H_2S \uparrow$$

Since formation of precipitates with $(NH_4)_2S$ is the most characteristic property of Group III cations, the Ti^{++++} ion should be included in that group.

In contrast to Ti^{++++}, the ions VO_3^-, MoO_4^{--}, and WO_4^{--} are not precipitated by $(NH_4)_2S$, but form thiosalts. For example, ammonium molybdate solution, $(NH_4)_2MoO_4$, turns brown on addition of $(NH_4)_2S$ owing to formation of a thiomolybdate:

$$(NH_4)_2MoO_4 + 4(NH_4)_2S + 4H_2O = (NH_4)_2MoS_4 + 8NH_4OH$$

Tungstates and vanadates** react similarly with $(NH_4)_2S$:

$$Na_2WO_4 + 4(NH_4)_2S + 4H_2O = Na_2WS_4 + 8NH_4OH$$

$$NaVO_3 + 3(NH_4)_2S + 3H_2O = NaVS_3 + 6NH_4OH$$

The thiosalts formed in this reaction are similar in properties to the thiosalts of arsenic, antimony and tin. Thus, they are all easily soluble in water and are decomposed by acids. In the case of $(NH_4)_2MoS_4$ the last reaction is represented by the equations

$$(NH_4)_2MoS_4 + 2HCl = H_2MoS_4 + 2NH_4Cl$$

$$H_2MoS_4 = \downarrow MoS_3 + H_2S \uparrow$$

---

* Compare the action of $(NH_4)_2S$ on aluminium and chromium salts.

** Like As, Sb and Sn, the elements Mo, W and V form oxythiosalts (i.e., products formed by partial replacement of oxygen by sulphur in molecules of oxysalts). Their formation causes a gradual change in the colour of the solutions.

The sulphide of sexivalent molybdenum, MoS_3, is formed as a dark brown precipitate. If this precipitate is treated with excess $(NH_4)_2S$ or Na_2S, it redissolves to form a thiosalt, e.g.,

$$MoS_3 + Na_2S = Na_2MoS_4$$

The WO_4^{--} and VO_3^- ions behave quite similarly. For example, the thiosalts formed by the action of ammonium (or sodium) sulphide on Na_2WO_4 and $NaVO_3$ are soluble in water and decomposed when boiled with acids to form the sulphides WS_3 (light brown) and V_2S_5 (brown).

Like MoS_3, these sulphides redissolve in $(NH_4)_2S$ or Na_2S to form thiosalts. In other words, V_2S_5, WS_3 and MoS_3, like the sulphides of arsenic, antimony and tin, are of acidic character; this is determined by the positions of these elements in the respective groups of the periodic system (the metalloid groups: vanadium in Group V, molybdenum and tungsten in Group VI).

On the basis of these properties, the ions VO_3^-, MoO_4^{--} and WO_4^{--} should be assigned to analytical Group V. However, they differ from the other ions of this group by their behaviour with H_2S.

Whereas the ions formed by As, Sb and Sn are precipitated by hydrogen sulphide in acid solutions, only MoO_4^{--} of the ions considered in this chapter is precipitated by H_2S:

$$(NH_4)_2MoO_4 + 2HCl + 3H_2S = \downarrow MoS_3 + 2NH_4Cl + 4H_2O$$

Owing to the formation of a colloidal solution of MoS_3, the precipitation is complete only if it is performed under pressure. The ions VO_3^- and WO_4^{--} are not precipitated by hydrogen sulphide at all.

Because of this action of H_2S on quinquevalent vanadium and sexivalent tungsten ions, only titanium and molybdenum are found in the groups to which they belong in the course of systematic analysis. The WO_4^{--} ion is precipitated by HCl as the sparingly soluble tungstic acid H_2WO_4 together with the silver subgroup and is thus separated from most other cations. In contrast to WO_4^{--}, the VO_3^- ion is not precipitated either by HCl or by hydrogen sulphide; the latter reduces it to the divanadyl ion $V_2O_2^{++++}$:

$$2VO_3^- + H_2S + 6H^+ = V_2O_2^{++++} + \downarrow S + 4H_2O$$

Subsequent action of $(NH_4)_2S$ in ammoniacal solution on the resultant solution precipitates the divanadyl ion in the form of the sulphide VOS together with the Group III cations.

In the present chapter we consider only the case of greatest practical interest (and the simplest), when the ions formed by titanium, vanadium, molybdenum and tungsten are present together with cations of analytical Group III and the Cu^{++} ion.

All these elements can exist in several states of oxidation. It follows that oxidation-reduction reactions should be important among their analytical reactions, especially as such reactions are usually accompanied by colour changes.

It must be remembered that often these reactions proceed rather slowly. Therefore if they do not occur at once the reaction mixture must be left to stand for some time.

The ions Ti^{++++}, VO_3^-, MoO_4^{--} and WO_4^{--} are colourless.

82. Reactions of the Ti^{++++} Ion

1. Ammonium sulphide forms a white precipitate of $Ti(OH)_4$ with the Ti^{++++} ion:

$$Ti(SO_4)_2 + 2(NH_4)_2S + 4H_2O = \downarrow Ti(OH)_4 + 2(NH_4)_2SO_4 + 2H_2S \uparrow$$

The precipitate is soluble in acids. On prolonged boiling it is converted into metatitanic acid H_2TiO_3, soluble with difficulty in dilute acids:

$$Ti(OH)_4 = H_2TiO_3 + H_2O$$

2. Caustic alkalies and ammonia solution also precipitate $Ti(OH)_4$. This reaction is used for separating Ti^{++++} ions from VO_3^- and MoO_4^{--}, which are not precipitated by alkalies.

3. Hydrolysis. $Ti(OH)_4$ has amphoteric properties, and its basic properties are very weak. Salts of quadrivalent titanium formed by strong acids are hydrolyzed to a considerable extent and have an acidic reaction. Salts of weak acids do not exist at all in aqueous solutions (compare Al and Cr). Therefore if a salt of a weak acid is added to a solution containing Ti^{++++} cations, $Ti(OH)_4$ is precipitated (or H_2TiO_3 if the solution is boiled). In the case of CH_3COONa we have:

$$4CH_3COONa + 4H_2O \rightleftarrows 4CH_3COOH + 4NaOH$$

$$Ti(SO_4)_2 + 4NaOH = \downarrow Ti(OH)_4 + 2Na_2SO_4$$

As already stated, $(NH_4)_2S$ acts similarly.

4. Reduction of Ti^{++++} to Ti^{+++}. Acidify a solution of a titanium (IV) salt with concentrated HCl, add a piece of metallic zinc, and leave to stand. The following reaction occurs:

$$2Ti^{++++} + Zn = 2Ti^{+++} + Zn^{++}$$

The reaction is accompanied by the appearance of a pale violet colour characteristic of the Ti^{+++} ion. This colour can be detected only after fairly prolonged interaction of the solution with Zn, and if the Ti^{++++} ion concentration is high enough.

5. **Hydrogen peroxide** in acid solution gives an orange-yellow colour due to the formation of pertitanic acid, which probably has the formula* $H_2[TiO_2(SO_4)_2]$. The reaction can be represented by the equation

$$Ti(SO_4)_2 + H_2O_2 = H_2[TiO_2(SO_4)_2]$$

This is one of the most characteristic tests for the Ti^{++++} ion.

6. **Spot Test.** Mix a drop of the unknown solution with a drop of chromotropic acid solution** on a filter paper or on a spot plate. A characteristic brownish red colour appears. The Fe^{+++} ion gives a green colour with the reagent. Therefore Fe^{+++} must first be reduced to Fe^{++} by means of $SnCl_2$. Carry out the test as follows. Put a drop of $SnCl_2$ followed by a drop of the solution to be tested for Ti^{++++} on a piece of filter paper. Put another drop of $SnCl_2$ on top, and then moisten the spot with chromotropic acid solution. A brown spot or ring is formed in the presence of Ti^{++++}. The reaction detects 2 μg of Ti^{++++}.

According to I. P. Alimarin, the sensitivity of the test is greatly increased if it is performed in almost neutral solution, for example in the presence of acetate buffer mixture (CH_3COOH + CH_3COONa).

83. Reactions of the VO_3^- Ion

1. **Acids** colour vanadates orange-yellow owing to formation of polyvanadic acids, e.g.,

$$6NaVO_3 + 6HCl = 6NaCl + H_4V_6O_{17} + H_2O$$

2. **Ammonium sulphide, $(NH_4)_2S$,** when added cautiously to a metavanadate solution forms a brown precipitate of the pentasulphide V_2S_5, which dissolves in excess to form a thiosalt:

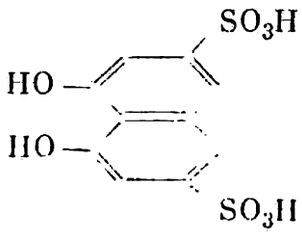
$$2NaVO_3 + 5(NH_4)_2S + 6H_2O = V_2S_5 + 10NH_4OH + 2NaOH$$

$$V_2S_5 + (NH_4)_2S = 2NH_4VS_3$$

3. **Hydrogen sulphide** in acid solution does not precipitate the VO_3^- ion but merely reduces it to the divanadyl ion $V_2O_2^{++++}$, which

* The formula $[TiO(H_2O_2)]SO_4$ is also ascribed to the reaction product.

** The formula of chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid) is



The composition of the compound formed with titanium is unknown. Chromotropic acid solutions are unstable; therefore they should be prepared in very small amounts.

is blue:

$$2NaVO_3 + H_2S + 6HCl = V_2O_2Cl_4 + \downarrow S + 2NaCl + 4H_2O$$

The reaction proceeds slowly in the cold and more rapidly on heating.

Certain other reducing agents, such as SO_2 or Fe^{++} ions, act similarly.

4. Reduction of VO_3^- to V^{+++} may be effected by the action of KI on an acidified vanadate solution, e.g.:

$$2NaVO_3 + 4KI + 6H_2SO_4 = V_2(SO_4)_3 + 2I_2 + Na_2SO_4 + 2K_2SO_4 + 6H_2O$$

The V^{+++} ion is green. However, the green colour becomes visible only after the solution has been boiled to remove the I_2 formed in the reaction.

5. Reduction of VO_3^- to V^{++} is effected by the action of metallic zinc on an acidified vanadate solution; the violet colour being characteristic of the V^{++} ion appears. The reaction is

$$2NaVO_3 + 3Zn + 12HCl = 2VCl_2 + 3ZnCl_2 + 2NaCl + 6H_2O$$

6. Formation of pervanadic acid, HVO_4. Add a drop of H_2O_2 solution to an acidified solution of a vanadate. The solution turns cherry-red or pinkish brown owing to the formation of pervanadic acid*:

$$NaVO_3 + H_2O_2 + HCl = HVO_4 + NaCl + H_2O$$

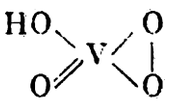
An excess of H_2O_2 weakens the colour and so lowers the sensitivity of the test.

7. Spot Test. Quinquevalent vanadium compounds are reduced by aniline in the presence of nitric acid to quadrivalent vanadium compounds, and the aniline is simultaneously oxidized to "aniline black". This reaction, proposed by N. A. Tananaev, is performed as follows. Put a drop of aniline hydrochloride $C_6H_5NH_2 \cdot HCl$ dissolved in concentrated HCl on a piece of filter paper, followed by a drop of the unknown solution previously acidified with concentrated HNO_3. In the presence of VO_3^- a black or blue-green (dependent on the vanadium concentration) spot or ring appears. The detectable minimum is 3 μg V.

8. Lignin. When a drop of metavanadate solution and a drop of phosphoric acid are placed on a piece of *newspaper* (which contains lignin), a black-green colour is formed instantly owing to reduction of quinquevalent vanadium to lower oxides. Nitric acid can be used

---

* Its structural formula is



instead of phosphoric, but the reaction is less effective. If filter paper, which does not contain lignin, is used instead of newspaper, a black-green colour is not formed.

84. Reactions of the MoO_4^{--} Ion

1. **Acids** form a white precipitate of molybdic acid, soluble in excess acid (distinction from tungsten), with molybdate solutions. When $(NH_4)_2MoO_4$ is evaporated with a few drops of concentrated H_2SO_4, a dark blue residue of a substance known as "molybdenum blue" is obtained; this is probably an intermediate oxide of molybdenum, with the formula $MoO_3 \cdot Mo_2O_5 \cdot xH_2O$, i.e., $Mo_3O_8 \cdot xH_2O$.

2. **Hydrogen sulphide, H_2S,** first turns acidified molybdate solutions blue owing to the formation of a colloidal solution of molybdenum blue, and then the brown sulphide is precipitated:

$$(NH_4)_2MoO_4 + 3H_2S + 2HCl = \downarrow MoS_3 + 2NH_4Cl + 4H_2O$$

Precipitation is complete only when H_2S acts under pressure. The MoS_3 precipitate dissolves in $(NH_4)_2S$ to form the thiosalt $(NH_4)_2MoS_4$. This salt can also be obtained by the action of $(NH_4)_2S$ on $(NH_4)_2MoO_4$. When the solution of the thiosalt is acidified, it decomposes into MoS_3 and H_2S (see Sec. 81 for the equations).

3. **Ammonium Thiocyanate, NH_4CNS, in the Presence of Stannous Chloride, $SnCl_2$.** When acidified $SnCl_2$ solution is added to a molybdate solution, Mo^{VI} is reduced to Mo^{V}; on subsequent addition of NH_4CNS (or KCNS) the latter forms the complex* $[MoO(CNS)_5]^{--}$, with a characteristic intense red colour.

The ionic form of the equation for this reaction is

$$2MoO_4^{--} + Sn^{++} + 12H^+ + 10CNS^- = 2[MoO(CNS)_5]^{--} + Sn^{++++} + 6H_2O$$

The Fe^{+++} ion gives a similar colour. However, this can be eliminated by addition of phosphoric acid, which binds the Fe^{+++} ion in the complex $[Fe(PO_4)_2]^{---}$. In the case of molybdenum the colour is not destroyed by H_3PO_4.

This reaction can be performed either in a test tube or as a spot test on paper. The latter is carried out as follows. Put a drop of acidified $SnCl_2$ solution on a strip of filter paper and treat the moist spot with the solution to be tested for molybdenum, such as $(NH_4)_2MoO_4$, followed by a drop of NH_4CNS solution. A red spot appears on the paper, owing to formation of $(NH_4)_2[MoO(CNS)_5]$.

---

* It has been shown by N. A. Tananaev and A. K. Babko that a complex of quinquevalent molybdenum is formed in this reaction. Formerly, this compound was regarded as a derivative of trivalent molybdenum, with the formula $[Mo(CNS)_6]^{---}$.

The colour is destroyed by concentrated HCl. In this case Fe^{+++} ions do not interfere, because they are reduced by $SnCl_2$ to Fe^{++} ions, which do not react with NH_4CNS. The test will detect 0.1 μg of Mo.

4. Action of Na_2HPO_4. Acidify 2-3 ml of $(NH_4)_2MoO_4$ solution with nitric acid, warm to about 50°, and add 0.5-1 ml of Na_2HPO_4 solution. A yellow crystalline precipitate of the ammonium salt of the complex phosphomolybdic acid $H_7[P(Mo_2O_7)_6]$ is formed:

$$12(NH_4)_2MoO_4 + Na_2HPO_4 + 23HNO_3 = \downarrow (NH_4)_3H_4[P(Mo_2O_7)_6] + \\ + 2NaNO_3 + 21NH_4NO_3 + 10H_2O$$

It will be remembered that an analogous precipitate of $(NH_4)_3H_4[As(Mo_2O_7)_6]$ is formed with the AsO_4^{---} ion, but only when the solution is heated almost to boiling.

5. Potassium xanthate* is the most sensitive and specific reagent for molybdenum. It gives an intense red colour with molybdates. If large amounts of molybdenum are present, almost black oily drops separate out.**

To a drop of neutral or weakly acidic solution containing molybdenum, placed on a spot plate, add a small grain of potassium xanthate and 2 drops of 2 *N* HCl. The test will detect 0.04 μg Mo.

Tartaric, citric and oxalic acids, and the cations Cu^{++}, Co^{++}, Ni^{++} and Bi^{+++} interfere with this test. The Ti^{++++} and VO_3^- ions do not interfere. WO_4^{--} must first be removed from the solution in the form of H_2WO_4.

In distinction from MoO_4^{--}, the Cu^{++} ion gives a yellow precipitate with xanthate (test this).

85. Reactions of the WO_4^{--} Ion

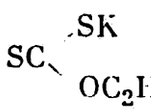
1. Acids. Concentrated mineral acids, such as HCl, precipitate white tungstic acid $H_2WO_4 \cdot H_2O$ from tungstate solutions:

$$Na_2WO_4 + 2HCl + H_2O = \downarrow H_2WO_4 \cdot H_2O + 2NaCl$$

On boiling, $H_2WO_4 \cdot H_2O$ is converted into the anhydrous acid H_2WO_4, yellow in colour. Tungstic acid is insoluble in concentrated

---

* Its formula is



** According to A. K. Babko, xanthate reduces Mo^{VI} to Mo^{V}, which forms the coloured xanthate complex. Part of the xanthate is oxidized to disulphide. The reaction may be represented by the equation

$$2MoO_4^{--} + 6C_2H_5OCS_2^- + 10H^+ = [Mo_2O_3(C_2H_5OCS_2)_4] + (C_2H_5OCS_2)_2 + 5H_2O$$

acids (distinction from H_2MoO_4). This reaction is used for separating WO_4^{--} from other ions.

2. **Hydrogen sulphide** does not form a precipitate with WO_4^{--} in acid solutions.

3. **Ammonium sulphide, $(NH_4)_2S$,** reacts with tungstates to form water-soluble thiosalts, e.g.,

$$Na_2WO_4 + 4(NH_4)_2S + 4H_2O = Na_2WS_4 + 8NH_4OH$$

Acids decompose the thiosalts to form a light brown precipitate of WS_3.

4. **Reduction of WO_4^{--} to W_2O_5.** (a) Add a small piece of metallic zinc to a tungstate solution acidified with HCl or H_2SO_4 in a porcelain basin or crucible and allow it to stand for some time. The tungstic acid which is first precipitated turns blue owing to reduction to W_2O_5. The reaction can be represented by the equation

$$2Na_2WO_4 + Zn + 6HCl = \downarrow W_2O_5 + ZnCl_2 + 4NaCl + 3H_2O$$

The reduction of tungsten proceeds further if zinc is present in excess and the acid concentration is high. The colour of the solution changes first to green and then to brown.

(b) The same compound (W_2O_5) is obtained when $SnCl_2$ solution is used instead of Zn:

$$2Na_2WO_4 + SnCl_2 + 6HCl = \downarrow W_2O_5 + SnCl_4 + 4NaCl + 3H_2O$$

In carrying out these experiments, the precipitate of tungstic acid prepared as described in 1 above can be used instead of Na_2WO_4 solution.

86. Analysis of Mixtures of the Ions Ti^{++++}, VO_3^-, MoO_4^{--}, WO_4^{--}

As already stated, we are not considering a general analytical scheme for cations which includes ions formed by titanium, tungsten, molybdenum and vanadium. We will discuss only the case of greatest practical interest, when ions formed by titanium, vanadium, molybdenum and tungsten are present together with Group III cations (except Zn^{++}) and Cu^{++}; this may occur in analysis of special steels and ferrous alloys.

The analytical procedure described below is based on the following principles: (a) H_2WO_4 is insoluble in water and in excess HCl; (b) MoO_4^{--} and Cu^{++} form precipitates with H_2S in acid solu-

tion; (c) Ti^{++++}, together with most Group III cations, is precipitated by excess caustic soda on heating while VO_3^- and AlO_2^- ions remain in solution.*

ANALYSIS OF A MIXTURE OF Ti^{++++}, VO_3^-, MoO_4^{--}, WO_4^{--} AND Cu^{++} IONS WITH GROUP III CATIONS (EXCEPT Zn^{++})

1. **Separation of WO_4^{--}.** Whether the solution contains a precipitate or not**, add about 1/5 of its own volume of concentrated HCl (sp. gr. 1.19) and boil for several minutes. WO_4^{--} is precipitated as free H_2WO_4 while all the other ions remain in solution (VO_3^- is converted into the yellow $V_6O_{17}^{=}$ ion). Allow the precipitate to settle, filter, wash it with hot water containing HCl, and investigate as described in 2. Examine the solution according to 3.

2. **Detection of WO_4^{--}.** Treat the precipitate with HCl in a test tube and add a piece of zinc metal or some $SnCl_2$ solution. Leave to stand if necessary. A blue precipitate of W_2O_5 indicates the presence of tungsten.

3. **Precipitation of Cu^{++} and MoO_4^{--}.** Add a few millilitres of $(NH_4)_2S_2O_8$ solution to the filtrate (or to the original solution if no precipitate forms on addition of HCl), warm to 60-70°, and pass H_2S. After 5-10 minutes dilute the solution with an equal volume of cold water and again saturate it with hydrogen sulphide. CuS, MoS_3 (partially) and sulphur are precipitated, and the ions of other elements (with some molybdenum) remain in solution. Filter off the precipitate, wash it with water containing a little HCl, and investigate as described in 4. The filtrate is investigated according to 5.

$(NH_4)_2S_2O_8$ is added in order to oxidize some hydrogen sulphide; the sulphur precipitate formed brings down with it MoS_3 from colloidal solution. The precipitation of molybdenum is nevertheless incomplete, but this does not interfere with subsequent analysis.

4. **Detection of Cu^{++} and MoO_4^{--}.** Transfer the precipitate of CuS and MoS_3 to a porcelain basin and dissolve on heating in the minimum amount of HNO_3 (sp. gr. 1.2) *in a fume cupboard.* Then add a few millilitres of 2 *N* H_2SO_4 and evaporate until thick white fumes of SO_3 appear (this is done to remove HNO_3, which would interfere during the subsequent detection of MoO_4^{--}). Allow the contents of the basin to cool, and dilute cautiously with several

---

* In the cold, Cr^{+++} would also pass into solution in the form of CrO_2^- ions. Chromites are hydrolyzed on heating to give a precipitate of $Cr(OH)_3$ (p. 269).

** The precipitate may contain tungstic acid and various compounds soluble in HCl, such as Group III hydroxides, carbonates, or sulphides, H_4TiO_4, etc.

millilitres of water. The solution may contain $CuSO_4$, H_2MoO_4 and H_2SO_4. Test separate portions for:

(a) Cu^{++} by the action of excess concentrated NH_4OH (see p. 357);

(b) MoO_4^{--} by the test with $SnCl_2$ and NH_4CNS, in a test tube or on a filter paper (Sec. 84, 3).

5. Precipitation of Ti^{++++} and Group III Cations. Boil out H_2S from the filtrate after separation of CuS and MoS_3 (*in a fume cupboard*). Filter off any precipitate formed (MoS_3 and S). Oxidize Fe^{++} and $V_2O_2^{++}$ (present in solution, and formed owing to reduction of quinquevalent vanadium by hydrogen sulphide) by boiling with a small amount of concentrated HNO_3. Neutralize excess acid by adding 25% NaOH solution until alkaline to litmus. Add a few more millilitres of NaOH, and boil for 10-15 minutes (beware of bumping).

On addition of NaOH the Ti^{++++} ion is first precipitated in the form of the acid-soluble $Ti(OH)_4$, which on boiling is gradually converted into metatitanic acid H_2TiO_3, which dissolves in acids with difficulty. The hydroxides of bivalent manganese, nickel and cobalt, and of trivalent iron and chromium are also precipitated. The solution contains aluminium as AlO_2^-, vanadium as VO_3^- (and some molybdenum as MoO_4^{--}) together with excess NaOH. Investigate the filtrate and precipitate as described in 9 and 6.

6. Separation of Ti^{++++} from Group III Cations. Wash the precipitate *thoroughly* with hot water and then treat it on the filter with cold 2 *N* sulphuric acid. This dissolves the Group III hydroxides and a small proportion of metatitanic acid, H_2TiO_3, the greater part of the latter remaining on the filter.

Further treatment of the precipitate and filtrate is described in 7 and 8.

7. Detection of Ti^{++++}. Treat the H_2TiO_3 precipitate on the filter with a mixture of 2 *N* H_2SO_4 (5 volumes) and H_2O_2 (1 volume). Orange-yellow pertitanic acid (Sec. 82, 5) is formed and passes into the filtrate*. Its formation indicates the presence of Ti^{++++} ions.

8. Detection of Fe^{+++}, Mn^{++}, Cr^{+++}, Co^{++}, and Ni^{++}. Test separate portions of the filtrate from 6 for the following ions:

(a) Fe^{+++} by the $K_4[Fe(CN)_6]$ test (p. 276);

(b) Mn^{++} by the test with $(NH_4)_2S_2O_8$ in the presence of $AgNO_3$ (p. 281), and Cr^{+++} as described in Sec. 54;

---

* As $Mn(OH)_2$ is readily oxidized in air, it may happen that all the manganese is present in the residue in the form of $MnO(OH)_2$, which is insoluble in H_2SO_4, together with H_2TiO_3, and not in the filtrate. However, it is dissolved by the action of sulphuric acid and hydrogen peroxide because Mn^{IV} is reduced to Mn^{II} by H_2O_2. Therefore the solution obtained by the action of these reagents should be kept and tested for Mn^{++} if it is not detected as described in 8.

Table 27

Analysis of Mixtures of Ti^{++++}, VO_3^-, MoO_4^{--}, WO_4^{--} and Cu^{++} with Group III Cations (in Absence of Zn^{++})

1. Separate WO_4^{--} and dissolve precipitate in concentrated HCl

Precipitate: $H_2WO_4 \cdot H_2O$ (white) or H_2WO_4 (yellow)

2. Test for WO_4^{--}

Filtrate: Ti^{++++}, $H_4V_6O_{17}$, MoO_4^{--}, Cu^{++}, Al^{+++}, Cr^{+++}, Fe^{+++}, Mn^{++}, Co^{++}, Ni^{++} (HCl)

3. Pass H_2S in the presence of $(NH_4)_2S_2O_8$ to precipitate Cu^{++} and MoO_4^{--}

Precipitate: CuS, MoS (S)

Filtrate: Ti^{++++}, $V_2O_2^{++++}$, (MoO_4^{--}), Cr^{+++}, Al^{+++}, Fe^{++}, Mn^{++}, Co^{++}, Ni^{++} (HCl, H_2S)

4. Dissolve ppt. in HNO_3. Evaporate with H_2SO_4 to remove excess HNO_3, dilute with water

5. Boil out H_2S. Heat with HNO_3 to oxidize Fe^{++} and $V_2O_2^{++++}$. Separate Ti^{++++} and Group III cations from Al^{+++} and VO_3^- by adding excess NaOH and boiling

Precipitate: H_2TiO_3, $[Ti(OH)_4]$, $Cr(OH)_3$, $Fe(OH)_3$, $Mn(OH)_2$, $MnO(OH)_2$ (part), $Co(OH)_2$, $Ni(OH)_2$

Filtrate: AlO_2^-, VO_3^-, MoO_4^{--} (part) (NaOH)

9. Test for:
(a) VO_3^-
(b) Al^{+++}
(in separate portions after acidifying with HCl)

Solution: Cu^{++}, MoO_4^{--} (H_2SO_4)
Test for:
(a) Cu^{++}
(b) MoO_4^{--}
(in separate portions)

6. Separate Ti^{++++} by the action of H_2SO_4

Precipitate: H_2TiO_3 and $MnO(OH)_2$

7. Test for Ti^{++++} with $H_2SO_4 + H_2O$

Filtrate: Cr^{+++}, Fe^{+++}, Mn^{++}, Co^{++}, Ni^{++} (H_2SO_4)

8. Test for:
(a) Fe^{+++}
(b) Mn^{++} and Cr^{+++}
(c) Co^{++}
(d) Ni^{++}

(c) Co^{++} by the test with NH_4CNS, with fluoride added to bind Fe^{+++} (p. 292);

(d) Ni^{++} by the dimethylglyoxime test, after precipitation of interfering cations (Fe^{+++}) by a *small* excess of ammonia (p. 296).

9. Detection of VO_3^- and Al^{+++}. Acidify the filtrate after separation of Ti^{++++} and Group III cations (see 5) with HCl until slightly acid to litmus, evaporate to a small volume, and test separate portions for:

(a) VO_3^- by adding about 0.5 ml of H_2O_2 (formation of cherry-red or pinkish brown pervanadic acid, HVO_4), or by the spot test with aniline (Sec. 83, 7);

(b) Al^{+++} by the action of NH_4OH or excess CH_3COONa (in the latter case, dilute with water and boil; see p. 265). Confirm by dissolving the precipitate in acetic acid and testing the solution for Al^{+++} with aluminon, alizarin, or morin.

The whole analytical procedure is shown schematically in Table 27.

QUESTIONS AND PROBLEMS

1. Where are Ti, V, Mo and W located in the periodic system? List thei most important oxides and acids.
2. To which analytical groups should the ions Ti^{++++}, VO_3^-, MoO_4^{--} and WO_4^{--} be assigned?
3. Describe the action of $(NH_4)_2S$ on the ions Ti^{++++}, VO_3^-, MoO_4^{--} and WO_4^{--}.
4. What is the action of acids on the thiosalts of vanadium (V), molybdenum (VI) and tungsten (VI)? Write equations for the reactions.
5. What is the action of H_2S on the ions VO_3^-, MoO_4^{--} and WO_4^{--} in acid solution?
6. Describe the action of caustic alkalies on Ti^{++++} in the cold and on boiling.
7. What is the action of salts of weak acids, such as Na_2CO_3 on solutions of quadrivalent titanium salts?
8. What is the action of H_2O_2 in the presence of H_2SO_4 on precipitated metatitanic acid? Write the equation for the reaction.
9. Describe the action of (a) acids; (b) H_2S in acid solution on VO_3^-. Describe the colour changes which occur.
10. What is the action of hydrogen peroxide on VO_3^- in acid solution?
11. Describe the spot tests for (a) Ti^{++++}; (b) VO_3^-.
12. What are the effects of (a) acids; (b) Na_2HPO_4 in the presence of HNO_3; (c) $SnCl_2$ and NH_4CNS on MoO_4^{--}?
13. Describe the separation and detection of the WO_4^{--} ion.
14. Describe the separation of Ti^{++++} from VO_3^- and Al^{+++}.

CHAPTER VIII

ANIONS

87. Classification of Anions

*The classification of anions is usually based on the different solubilities of the barium and silver salts of the respective acids**. This is not a rigorous classification, because different authors subdivide the anions into different numbers of groups. We will subdivide them into only three groups, as shown in Table 28.

In contrast to the cations, most anions do not interfere in tests for other anions. Therefore separation reactions are rarely needed. More usually anions are detected by the fractional method, in separate portions of the unknown solution. Accordingly, the group reagents in anion analysis are generally used merely for detection and not separation of the groups. It is obvious that if a particular group is shown to be absent there is no point in testing for the individual anions in it. Group reactions therefore make the analysis much easier.

We have already met most of the reactions of the anions in our study of the cations. For example, the cations Ba^{++} and Pb^{++} were detected by means of the anions SO_4^{--} and CrO_4^{--}. Conversely, the two latter can be detected with the aid of barium and lead salts. Similarly, the Cl^- ion is the reagent for Ag^+ and, conversely, Cl^- can be detected by means of Ag^+, etc.

FIRST GROUP OF ANIONS

Anions of Group I include: sulphate, SO_4^{--}, sulphite, SO_3^{--}, thiosulphate, $S_2O_3^{--}$, carbonate, CO_3^{--}, phosphate, PO_4^{---}, arsenate,** AsO_4^{---}, arsenite, AsO_3^{---}, borate, BO_2^- or $B_4O_7^{--}$, chromate, CrO_4^{--}, fluoride, F^-, silicate, SiO_3^{--}, oxalate, $C_2O_4^{--}$, and

---

* Classifications based on other principles are also used. For example, N. A. Tananaev uses the following classification. Group I—oxidizing anions (MnO_4^-, CrO_4^{--}, NO_3^-, NO_2^-, AsO_4^{---}, $[Fe(CN)_6]^{---}$, etc.); Group II—reducing anions (Cl^-, Br^-, I^-, S^{--}, SO_3^{--}, $S_2O_3^{--}$, CNS^-, AsO_3^{---}, $[Fe(CN)_6]^{==}$, $C_2O_4^{--}$, etc.); Group III—indifferent anions (SO_4^{--}, PO_4^{---}, BO_2^-, SiO_3^{--}, CO_3^{--}, F^-, CH_3COO^-, etc.).

** See Sec. 76 for the reactions of AsO_4^{---} and AsO_3^{---} and Sec. 54 for the reactions of CrO_4^{--}.

Table 28

Classification of Anions

Group number	Group characteristics	Anions in group	Group reagent
I	Barium salts sparingly soluble in water	SO_4^{--} (sulphate) SO_3^{--} (sulphite) $S_2O_3^{--}$ (thiosulphate) CO_3^{--} (carbonate) PO_4^{---} (phosphate) AsO_4^{---} (arsenate) AsO_3^{---} (arsenite) BO_2^- or $B_4O_7^{--}$ (borate) CrO_4^{--} (chromate) F^- (fluoride) SiO_3^{--} (silicate) $C_2O_4^{--}$ (oxalate), etc.	$BaCl_2$ in neutral or weakly alkaline solution
II	Silver salts sparingly soluble in water and dilute HNO_3 *	Cl^- (chloride) Br^- (bromide) I^- (iodide) S^{--} (sulphide) CNS^- (thiocyanate) $[Fe(CN)_6]^{==}$ (ferrocyanide) $[Fe(CN)_6]^{---}$ (ferricyanide) and others	$AgNO_3$ in presence of HNO_3
III	Barium and silver salts soluble in water	NO_3^- (nitrate) NO_2^- (nitrite) CH_3COO^- (acetate) MnO_4^- (permanganate)	No group reagent

* Silver sulphide dissolves in HNO_3 on heating.

others. *These anions react with* Ba^{++} *ions to give salts which are sparingly soluble in water, but (with the exception of* $BaSO_4$*) are soluble in acids.* Therefore Group I anions are not precipitated as barium salts from acid solutions.

Accordingly, the anion Group I reagent is barium chloride in neutral or slightly alkaline solution (pH = 7-9).

The salts formed by Group I anions with Ag^+, in distinction from Group II anions, are soluble in dilute acids or even in water (Ag_2SO_4 and AgF).

88. Reactions of Sulphate, SO_4^{--}

The sulphate ion is the anion of sulphuric acid, H_2SO_4. This is a strong acid, somewhat weaker only than the halide acids HCl. HBr, HI, and nitric acid.

Barium, strontium, and lead sulphates are sparingly soluble in water; the calcium salt is somewhat more soluble. The remaining sulphates are easily soluble.

Solutions of Na_2SO_4 and K_2SO_4 are neutral, but 0.1 *N* $NaHSO_4$ and $KHSO_4$ solutions are acidic (pH $\approx$ 2). The SO_4^{--} ion is colourless.

1. Barium chloride (the Ba^{++} ion) reacts with solutions containing the SO_4^{--} ion to give a white precipitate of $BaSO_4$. Being an insoluble salt of a strong acid, barium sulphate *is not dissolved by acids.* This distinguishes $BaSO_4$ from all other barium salts, and this fact is used as a test for SO_4^{--}. The test is complicated somewhat if the solution contains the $S_2O_3^{--}$ anion or a mixture of SO_3^{--} and S^{--} ions, as in both cases addition of acid produces a white precipitate of sulphur which, like $BaSO_4$, is insoluble in acids:

$$S_2O_3^{--} + 2H^+ = \downarrow S + SO_2 + H_2O$$

$$2S^{--} + SO_3^{--} + 6H^+ = \downarrow 3S + 3H_2O$$

$BaSO_4$ can be distinguished from sulphur, as it forms mixed crystals of pink colour with $KMnO_4$.

To 2-3 ml of the unknown solution, acidified with HCl, add 5 ml of 0.01 *N* $KMnO_4$ and some $BaCl_2$ solution. Reduce excess $KMnO_4$ by adding H_2O_2; the solution becomes decolourized (p. 282) and the precipitate is pink. This shows the presence of $BaSO_4$. The $KMnO_4$ trapped by the latter does not react with hydrogen peroxide because it is inside the $BaSO_4$ crystals.

2. Strontium salts (the Sr^{++} ion) give a white precipitate of $SrSO_4$, insoluble in acids.

3. Lead salts (the Pb^{++} ion) give a white precipitate of $PbSO_4$, soluble in caustic alkalies and in ammonium acetate (Sec. 68).

4. Silver nitrate, $AgNO_3$, does not form a precipitate with dilute solutions of sulphates, as Ag_2SO_4 is fairly soluble in water. However, in concentrated sulphate solutions Ag_2SO_4 (white) may be precipitated.

5. Microcrystalloscopic Test. Add a small drop of $(CH_3COO)_2Ca$ or $Ca(NO_3)_2$ solution to the solution being tested for SO_4^{--} and warm until a border forms. Crystals of calcium sulphate dihydrate (gypsum), $CaSO_4 \cdot 2H_2O$, are formed (see Figs. 23 and 24). The detectable minimum is 0.035 μg SO_4^{--}.

This test should be used only if SO_3^{--}, $S_2O_3^{--}$ and S^{--} are known to be absent; otherwise, because these ions are easily oxidized, the SO_4^{--} ion may be found in error.

89. Reactions of Sulphite, SO_3^{--}

Sulphite is the anion of sulphurous acid, H_2SO_3. Anhydrous H_2SO_3 is unknown. When obtained in the pure state, it partially decomposes into its anhydride and water. Solutions of SO_2 in water have an acidic reaction and contain free H_2SO_3, which is a moderately strong acid.

Of its salts, only the alkali sulphites are soluble in water. The remaining sulphites are more or less insoluble in water, but dissolve in acids such as HCl. Aqueous solutions of Na_2SO_3 and K_2SO_3 have an alkaline reaction owing to hydrolysis (pH $\approx$ 9). On the other hand, the bisulphites of the same metals are weakly acidic in solution (pH = 4-5).

Sulphites are gradually oxidized to sulphates in aqueous solutions. The SO_3^{--} anion is colourless.

1. **Barium chloride** forms a white precipitate of $BaSO_3$ with the SO_3^{--} ion; the precipitate dissolves in acids with evolution of SO_2, e.g.,

$$BaSO_3 + 2HCl = BaCl_2 + H_2SO_3$$

$$H_2SO_3 = H_2O + SO_2 \uparrow$$

Sulphur dioxide, SO_2, is recognized by the characteristic smell of burning sulphur and by its ability to decolourize $KMnO_4$ or iodine solutions (see below).

2. **Silver nitrate, $AgNO_3$,** gives a white precipitate of Ag_2SO_3, soluble in HNO_3, with sulphite solutions.

3. **Strontium salts (the Sr^{++} ion)** form a white precipitate of $SrSO_3$ with sulphite solutions (distinction from $S_2O_3^{--}$).

4. **Acids** decompose all sulphites (soluble or insoluble in water) with evolution of SO_2. The action of acids on insoluble sulphites was discussed above (see 1). Now carry out the reaction with Na_2SO_3 solution. The equation is

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2 \uparrow$$

The detection of SO_2 is based on its ability to decolourize iodine or $KMnO_4$ solutions. The reaction between SO_2 and iodine is

$$SO_2 + I_2 + 2H_2O = 4H^+ + SO_4^{--} + 2I^-$$

Potassium permanganate, $KMnO_4$, oxidizes SO_2 partially to sulphuric acid and partially to dithionic acid, $H_2S_2O_6$. The equa-

tions are

$$5SO_2 + 2KMnO_4 + 2H_2O = 2KHSO_4 + 2MnSO_4 + H_2SO_4$$
$$6SO_2 + 2KMnO_4 + 2H_2O = 2KHSO_4 + 2MnSO_4 + H_2S_2O_6$$

Perform this experiment as follows. Put the solution to be tested for SO_3^{--}, such as Na_2SO_3, into a test tube fitted with a gas outlet tube (Fig. 42), add some HCl or H_2SO_4, immerse the test tube into a beaker with boiling water and pass the gas evolved through dilute $KMnO_4$ solution. It is more convenient to use very dilute iodine solution coloured blue by addition of starch solution, instead of potassium permanganate. SO_2 reduces I_2 to HI and the blue colour disappears.

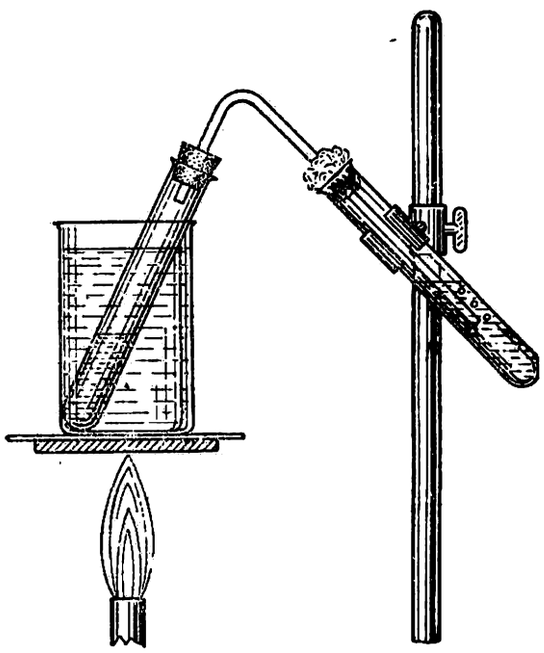


Fig. 42. Apparatus for detection of SO_3^{--} (and CO_3^{--}) ions

The solutions of $KMnO_4$ or iodine must be very dilute to ensure that the decolourization is rapid and that the test is sensitive (take not more than one drop of the laboratory solutions of $KMnO_4$ or iodine to half a test tube of water).

Thiosulphates also evolve SO_2 when acidified (Sec. 90). Sulphides give off H_2S when acidified, and this also decolourizes iodine and $KMnO_4$ solutions. Therefore the test described above is not applicable in the presence of $S_2O_3^{--}$ or S^{--}.

5. Reduction Reactions of SO_3^{--} Ions. Iodine is reduced by sulphite solutions as well as by gaseous SO_2, e.g.,

$$SO_3^{--} + I_2 + H_2O = SO_4^{--} + 2I^- + 2H^+$$

The solution becomes acidic, and this is an additional sign of the presence of SO_3^{--}. No acid is formed when $S_2O_3^{--}$ or S^{--} ions reduce iodine.*

Sulphites also reduce permanganate, both in acid and in alkaline solution. For example, when $KMnO_4$ solution is added drop by drop to Na_2SO_3 solution acidified with sulphuric acid it is decolourized

---

* The equations are

$$2S_2O_3^{--} + I_2 = 2I^- + S_4O_6^{--} \text{ (tetrathionate)}$$
$$S^{--} + I_2 = 2I^- + \downarrow S$$

(reduced to Mn^{++} ions):

$$5SO_3^{--} + 2MnO_4^- + 6H^+ = 5SO_4^{--} + 2Mn^{++} + 3H_2O$$

The reaction takes a different course in alkaline solution. The purple colour of the MnO_4^- ion first changes to green owing to formation of the manganate ion MnO_4^{--}, corresponding to sexivalent manganese. If the green solution is heated, it turns brown and a brown precipitate of $MnO(OH)_2$ is formed (see p. 332 with reference to oxidation by permanganate in acid and alkaline solutions). The reaction can be represented by the equation

$$3SO_3^{--} + 2MnO_4^- + 3H_2O = \downarrow 2MnO(OH)_2 + 3SO_4^{--} + 2OH^-$$

Many other reducing anions, such as S^{--}, $S_2O_3^{--}$, AsO_3^{---}, CNS^-, $[Fe(CN)_6]^{==}$ and I^-, reduce permanganate to $MnO(OH)_2$ in alkaline solution. This reaction is used in analysis as a preliminary test for these ions. It is also advisable to test another portion of the same solution with iodine solution in the presence of H_2SO_4 or HCl. The decolourization of I_2 indicates the presence of the strongest of the above-named reducing agents, namely, S^{--}, SO_3^{--} and $S_2O_3^{--}$.

6. Reduction of the SO_3^{--} Ion. As sulphur is in an intermediate valency state (+4) in the SO_3^{--} ion, the valency can be both increased and decreased. In other words, the SO_3^{--} ion can be reduced as well as oxidized. The reduction products of SO_3^{--} may be sulphur or H_2S. Study these reactions experimentally.

(a) Mix solutions of Na_2SO_3 and Na_2S and acidify the mixture with hydrochloric or sulphuric acid. Free sulphur is precipitated as the result of reduction of hydrogen sulphide by sulphurous acid, which is itself reduced to sulphur:

$$2H_2S + H_2SO_3 = \downarrow 3S + 3H_2O$$

(b) Add excess 2 *N* HCl and a piece of zinc metal to a sulphite solution, and heat. H_2S is evolved and may be detected by its smell or by the blackening of paper moistened with $(CH_3COO)_2Pb$ or Na_2PbO_2 solution. The equations are:

in the test tube

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2$$

$$3Zn + 6HCl + SO_2 = 3ZnCl_2 + 2H_2O + H_2S \uparrow$$

on the test paper

$$H_2S + (CH_3COO)_2Pb = \downarrow PbS + 2CH_3COOH$$

7. Decolourization of Fuchsin or Malachite Green. Sulphites can decolourize solutions of certain organic dyes, such as fuchsin or malachite green; this can be used as a test for SO_3^{--}.

Add a drop of the *neutral* unknown solution to a drop of solution of fuchsin or malachite green (or of a mixture of the two). The solution is decolourized in the presence of SO_3^{--}.

Acidic solutions are previously neutralized by addition of $NaHCO_3$; alkaline solutions are saturated with CO_2 until the colour due to a drop of phenolphthalein fades.

The S^{--} ion also decolourizes the above-named dyes and interferes in the test.

8. Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, gives a rose-red colour with neutral sulphite solutions. The colour is intensified by addition of excess $ZnSO_4$ solution. A red precipitate is formed if a drop of $K_4[Fe(CN)_6]$ is then added. The chemistry of this reaction is not yet understood. Acids destroy the colour; therefore acid solutions must be neutralized. The $S_2O_3^{--}$ ion does not give this reaction. The S^{--} ion gives a violet colour with sodium nitroprusside and therefore interferes with detection of SO_3^{--}.

90. Reactions of Thiosulphate, $S_2O_3^{--}$

The thiosulphate ion is the anion of thiosulphuric acid, $H_2S_2O_3$. This acid is even less stable than H_2SO_3 and decomposes into SO_2 and S when formed in the free state. The thiosulphates of the alkali metals, strontium, zinc and cadmium are soluble in water. The remaining thiosulphates are sparingly soluble. The $S_2O_3^{--}$ ion is colourless. Aqueous solutions of alkali thiosulphates are nearly neutral.

1. Barium chloride, $BaCl_2$, added in excess, forms a white precipitate of BaS_2O_3 with the $S_2O_3^{--}$ anion. As barium thiosulphate readily forms supersaturated solutions, the walls of the test tube should be rubbed with a glass rod.

2. Silver nitrate, $AgNO_3$, added in excess, gives a white precipitate of $Ag_2S_2O_3$, which rapidly turns yellow, then brown, and finally black owing to conversion into silver sulphide:

$$Ag_2S_2O_3 + H_2O = \downarrow Ag_2S + H_2SO_4$$

This is one of the most characteristic reactions of the $S_2O_3^{--}$ ion. It must be remembered that the $Ag_2S_2O_3$ precipitate dissolves in excess thiosulphate to form the complex ions $[Ag(S_2O_3)]^-$ and $[Ag_2(S_2O_3)_3]^{=-}$. Therefore the precipitate can form only if Ag^+ ions are present in excess.

3. Acids liberate free $H_2S_2O_3$ from solutions of thiosulphates; the free acid decomposes into H_2O, SO_2 and sulphur:

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2S_2O_3$$

$$H_2S_2O_3 = H_2O + SO_2\uparrow + \downarrow S$$

The sulphur formed in the reaction makes the solution turbid; the turbidity appears more rapidly at higher concentrations and temperatures. As sulphites liberate SO_2 without formation of sulphur (which makes the solution turbid in the case of thiosulphates) under the same conditions, this reaction can be used for detecting $S_2O_3^{--}$ in the presence of SO_3^{--}, and is one of the most important reactions of the thiosulphate ion.

4. **Iodine solution** is decolourized by solutions of thiosulphates, with formation of tetrathionates (salts of tetrathionic acid, $H_2S_4O_6$), e.g.:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

The reaction of iodine with thiosulphate is very important in quantitative analysis.

5. **Potassium permanganate, $KMnO_4$,** is reduced by thiosulphates to Mn^{++} cations in acid solutions, and to $MnO(OH)_2$, forming a brown precipitate, in alkaline solutions. Sulphates and tetrathionates are formed in these reactions.

6. **Ferric chloride** gives a deep violet colour with thiosulphate solutions. The colour quickly disappears; it is probably due to the formation of ferric thiosulphate (or a corresponding complex). The colour fades owing to reduction of ferric iron to ferrous:

$$2Fe^{+++} + 2S_2O_3^{--} = 2Fe^{++} + S_4O_6^{--}$$

91. Reactions of Carbonate, CO_3^{--}

The carbonate ion is the anion of carbonic acid, H_2CO_3, which is unknown in the free state. When formed from its salts, it decomposes almost completely into the anhydride (CO_2) and water. As H_2CO_3 is a very weak acid, carbonates of the alkali metals have an alkaline reaction. The only neutral carbonates soluble in water are those of potassium, sodium and ammonium. Cations of all other groups are precipitated by the CO_3^{--} ion in the form of neutral and basic salts, and some (such as Al^{+++}, Cr^{+++}, Ti^{++++}) as the hydroxides. As the result of hydrolysis, 0.1 *N* Na_2CO_3 and K_2CO_3 solutions have a strongly alkaline reaction (pH = 11.6). The CO_3^{--} ion is colourless.

1. **Barium chloride, $BaCl_2$,** precipitates the CO_3^{--} ion in the form of white $BaCO_3$, which dissolves in HCl, HNO_3 and CH_3COOH with evolution of CO_2. The action of H_2SO_4 converts barium carbonate into the even less soluble barium sulphate.

2. **Silver nitrate, $AgNO_3$,** forms a white precipitate of Ag_2CO_3, soluble in acids. HCl converts it into AgCl.

3. **Acids** decompose all carbonates with evolution of CO_2 (effervescence), e.g.,

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2CO_3$$
$$H_2CO_3 = H_2O + CO_2 \uparrow$$

The evolution of CO_2 can be detected by means of lime or baryta water, i.e., $Ca(OH)_2$ or $Ba(OH)_2$ solutions, which are turned turbid by CO_2 owing to precipitation of $CaCO_3$ or $BaCO_3$:

$$CO_2 + Ca(OH)_2 = \downarrow CaCO_3 + H_2O$$

The apparatus shown in Fig. 42 (p. 432) can be used for this test. The apparatus shown in Fig. 43 is even more convenient. Put a small amount of the solution (or solid) to be tested into the test tube *1* and add dilute H_2SO_4 from the dropping funnel *2*. Immerse the end of the outlet tube *3* into $Ca(OH)_2$ or $Ba(OH)_2$ solution* in the test tube *4*. Put the test tube *1* into a beaker with hot water for a few minutes. If no turbidity appears in the liquid in test tube *4*, fill test tube *1* with hot distilled water from the funnel. This would displace any CO_2 out of test tube *1* and pass it through the solution in test tube *4*.

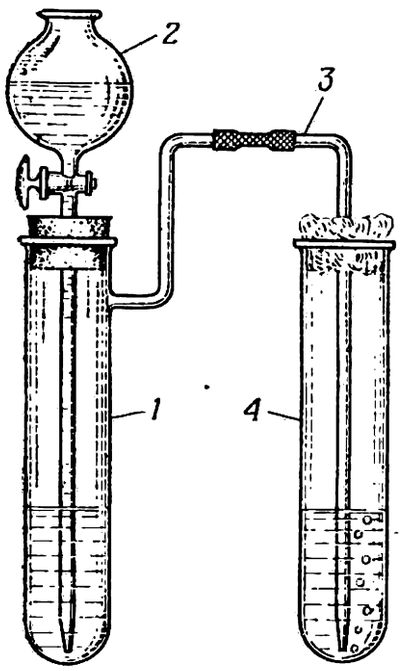


Fig. 43. Apparatus for detection of CO_3^{--} ions
1, *4*—test tubes; *2*—dropping funnel; *3*—gas outlet tube

It should be remembered that lime water may be turned very slightly cloudy by carbon dioxide from the air present in the test tube. If $Ba(OH)_2$ is used, the turbidity can be quite appreciable. It is therefore better to use $Ca(OH)_2$ solution. The solution must first be tested.**

It must be borne in mind that the turbidity due to $CaCO_3$ or $BaCO_3$ which appears initially may disappear after some time by the action of excess CO_2 owing to the formation of a soluble bicarbonate:

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$

4. Detection of CO_3^{--} in the presence of SO_3^{--} and $S_2O_3^{--}$. The presence of SO_3^{--} or $S_2O_3^{--}$ ions interferes with detection of CO_3^{--}, because the SO_2 evolved by the action of acids on sulphites and thiosulphates is absorbed by $Ca(OH)_2$ and can form a white precipitate of $CaSO_3$. Therefore if these ions have been found, they must be oxidized. Excess H_2O_2 solution is added for this purpose before addition of H_2SO_4. The test is then performed as described above (see 3). Other oxidizing agents, such as $KMnO_4$ or $K_2Cr_2O_7$, can be used instead of hydrogen peroxide.

---

* The solution must be absolutely clear.

** For example, air can be blown through the lime water from the mouth with the aid of a glass tube.

92. Reactions of Phosphate, PO_4^{---}

The phosphate ion, PO_4^{---}, is the anion of orthophosphoric acid, H_3PO_4, which is an acid of moderate strength. Being a tribasic acid, it forms three series of salts:

Phosphates: Na_3PO_4, $Ca_3(PO_4)_2$, etc.

Monohydrogen phosphates: Na_2HPO_4, $CaHPO_4$, etc.

Dihydrogen phosphates: NaH_2PO_4, $Ca(H_2PO_4)_2$, etc.

The only salts of H_3PO_4 to be soluble in water are those of the alkali metals and ammonium, and the dihydrogen phosphates of the alkaline earth, such as $Ca(H_2PO_4)_2$. The other salts are sparingly soluble in water, but dissolve in mineral acids, and many also in acetic acid; $FePO_4$ and $AlPO_4$ are insoluble in acetic acid. The bismuth salt, $BiPO_4$, dissolves with difficulty in dilute (0.5 *N*) HNO_3. Phosphates of the alkali metals have a strongly alkaline reaction. The calculated pH value for 0.1 *M* Na_3PO_4 solution is 12.8. At the same concentration, the pH of Na_2HPO_4 is 9.9, and that of NaH_2PO_4 is 4.6 (see Table 15, p. 216). The PO_4^{---} ion is colourless.

Use a solution of Na_2HPO_4 for studying its reactions.

1. **Barium chloride** reacts with Na_2HPO_4 solution to give a white precipitate of $BaHPO_4$, soluble in acids (except H_2SO_4):

$$Ba^{++} + HPO_4^{--} = \downarrow BaHPO_4$$

In the presence of alkalies or NH_4OH the HPO_4^{--} ion is converted into PO_4^{---}:

$$HPO_4^{--} + OH^- = PO_4^{---} + H_2O$$

The precipitate is then $Ba_3(PO_4)_2$:

$$3Ba^{++} + 2PO_4^{---} = \downarrow Ba_3(PO_4)_2$$

The effect of acids on it is the same as on $BaHPO_4$.

2. **Silver nitrate** gives a white precipitate of Ag_3PO_4, soluble in HNO_3 and NH_4OH. It will be remembered that the AsO_4^{---} ion, very similar to PO_4^{---} in properties, gives a chocolate-brown precipitate of Ag_3AsO_4 with Ag^+.

3. **Magnesia mixture**, which is a mixture of $MgCl_2$ with NH_4OH and NH_4Cl, gives a white crystalline precipitate of $MgNH_4PO_4$:

$$HPO_4^{--} + NH_4OH + Mg^{++} = \downarrow MgNH_4PO_4 + H_2O$$

This reaction was discussed in Sec. 22 (p. 100). It can also be used as a microcrystalloscopic test for PO_4^{---}. Add one drop each of NH_4OH and NH_4Cl solutions followed by a small crystal of $MgSO_4$ to the solution under test. Characteristic crystals of $MgNH_4PO_4 \cdot 6H_2O$

are formed (see Figs. 12 and 13, p. 101). The detectable minimum is 0.01 μg PO_4^{---}. The dilution limit is 1:66,000.

Remember that the AsO_4^{---} ion forms similar crystals. In distinction from AsO_4^{---}, the AsO_3^{---} ion does not form a precipitate with magnesia mixture except when present at high concentrations.

4. **Ammonium molybdate,** a solution of $(NH_4)_2MoO_4$ in HNO_3, forms a characteristic yellow crystalline precipitate of ammonium phosphomolybdate with phosphates; its formula* is $(NH_4)_3H_4[P(Mo_2O_7)_6]$.

The equation for the reaction is

$$PO_4^{---} + 3NH_4^+ + 12MoO_4^{--} + 24H^+ = \downarrow (NH_4)_3H_4[P(Mo_2O_7)_6] + 10H_2O$$

Like the precipitate formed by the AsO_4^{---} ion, the precipitate of ammonium phosphomolybdate dissolves in excess phosphate to form complex anions. The reagent must therefore be taken *in large excess.* To 2-3 ml of ammonium molybdate solution heated to 50-60° add about one fifth of its volume of the phosphate solution drop by drop. Allow it to stand if necessary. The sensitivity is increased by addition of solid NH_4NO_3 (the common NH_4^+ ions lower the solubility of the precipitate).

Reducing agents, such as SO_3^{--}, $S_2O_3^{--}$, S^{--} ions, etc., interfere, as they reduce Mo^{VI} to "molybdenum blue" ($Mo_3O_8 \cdot xH_2O$). The solution therefore turns blue. Large amounts of chlorides should also be avoided. To oxidize reducing agents and to remove a part of the Cl^- ions, 1-2 ml of the unknown solution should be boiled with 2-3 ml of concentrated HNO_3 before the test is performed as described above.

5. **Spot Test.** As was pointed out in the discussion of complex compounds (p. 240), sexivalent molybdenum in complexes with AsO_4^{---} or PO_4^{---} ions is more reactive and can oxidize substances which are not oxidized by simple molybdates. Such substances include benzidine, $C_{12}H_8(NH_2)_2$, already mentioned a number of times, which is oxidized to blue compounds; the "molybdenum blue" formed in the reaction also has a blue colour. Because of this, and also owing to the fact that one phosphate molecule binds and therefore activates $12MoO_3$ molecules, the reaction between $(NH_4)_3H_4[P(Mo_2O_7)_6]$ and benzidine is very sensitive. It is carried out as follows. Put a drop of the acidified solution to be tested for PO_4^{---} on a piece of ashless filter paper, followed by a drop of ammonium molybdate solution and then a drop of benzidine. To lower the activity of the solution, hold the paper in ammonia vapour or treat the spot with a drop of CH_3COONa. A blue colour appears

---

* More precisely, $(NH_4)_3(H_3O)_4[P(Mo_2O_7)_6]$.

in the presence of PO_4^{---}; its intensity depends on the PO_4^{---} concentration.

The AsO_4^{---} ion does not react under these conditions, because the formation of $(NH_4)_3H_4[As(Mo_2O_7)_6]$ in the cold is very slow. However, the SiO_3^{--} ion forms a similar (although soluble) salt;

Table 29

Analysis of Mixtures of PO_4^{---}, AsO_4^{---} and AsO_3^{---} Anions

1. Separation of AsO_4^{---} and PO_4^{---} from AsO_3^{---}. Add a small amount of 2 *N* NH_4Cl and NH_4OH (until the liquid smells of ammonia) followed by a solution of a magnesium salt. If no precipitate forms, rub the walls of the tube with a glass rod and leave to stand. After 15 minutes filter off the precipitate and wash with water containing a little NH_4OH (to lower the solubility of the precipitate)

Filtrate: AsO_3^{---} (and other anions)	*Precipitate:* $MgNH_4AsO_4$, $MgNH_4PO_4$ and other magnesium salts **
2. Test for AsO_3^{---}. Acidify with 2 *N* HCl, heat, pass H_2S. Rapid formation of yellow As_2S_3 precipitate *, soluble in NH_4OH and reprecipitated by acid, indicates presence of AsO_3^{---}	3. Tests for AsO_4^{---} and PO_4^{---}. Dissolve the precipitate in 2 *N* acetic acid and test separate portions for AsO_4^{---} and PO_4^{---} (a) AsO_4^{---}. Acidify a portion of the solution with an equal volume of concentrated HCl (sp. gr. 1.19) and add a few drops of KI solution *** and 1-2 ml of benzene, C_6H_6. Appearance of a violet colour (on shaking) in the benzene layer (due to I_2) indicates the presence of AsO_4^{---} ions **** (b) PO_4^{---}. Test for PO_4^{---} by the spot test with $(NH_4)_2MoO_4$ in presence of tartaric acid (Sec. 92, 5). In absence of AsO_4^{---}, the ammonium molybdate test in presence of HNO_3 (Sec. 92, 4) can be used for detecting PO_4^{---}

* Very slow precipitation of As_2S_3 may be due to incomplete precipitation of AsO_4^{---} in the form of $MgNH_4AsO_4$ (slow reduction of AsO_4^{---} to AsO_3^{---}, followed by precipitation with hydrogen sulphide; see p. 387).

** Formed owing to the presence of other anions in the unknown solution.

*** The KI solution must be free from KIO_3.

**** This test is unreliable in the presence of oxidizing agents (NO_2^-, CrO_4^{--}) which may be coprecipitated with $MgNH_4AsO_4$ and $MgNH_4PO_4$. In such cases acidify part of the solution with an equal volume of concentrated HCl and pass H_2S. A yellow precipitate of As_2S_5 indicates the presence of AsO_4^{---}.

small amounts of this ion may always be present as the result of extraction of traces of silicates from the glass. It is therefore preferable to carry out the test in the presence of tartaric acid, which prevents the formation of silico- and arsenomolybdates, because it forms very stable complexes with molybdic acid. On the other hand, phosphomolybdic acid is formed even in the presence of tartaric acid.

The test for PO_4^{---} by this method is performed as described above, except that ammonium molybdate solution containing tartaric acid is used as the reagent. Before addition of CH_3COONa (or treatment with NH_3 vapour) it is advisable to hold the spot over heated wire gauze to speed up the reaction. The test detects 1.5 μg PO_4^{---} in the presence of 500 times the amount of silicic acid.

6. Detection of PO_4^{---}, AsO_4^{---} and AsO_3^{---} ions present simultaneously. This is performed as shown in Table 29.

93. Reactions of Borate Ions, $B_4O_7^{--}$ and BO_2^-

Free boric (orthoboric) acid, H_3BO_3, is a white crystalline solid, fairly easily soluble in water, and is one of the weakest acids. However, the salts of boric acid (borates) correspond to metaboric acid, HBO_2, or to tetraboric acid, $H_2B_4O_7$, and not to H_3BO_3.

Only the alkali borates are soluble in water. The most important is sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$, known as borax. Being salts of a very weak acid, all soluble borates are strongly hydrolyzed in aqueous solution and have an alkaline reaction. Borates which are not soluble in water dissolve in acids. Solutions of borates are colourless.

1. Barium chloride forms a white precipitate of barium metaborate, $Ba(BO_2)_2$, with not excessively dilute $Na_2B_4O_7$ solutions. Its formation may be represented as follows:

$$B_4O_7^{--} + 3H_2O \rightleftarrows 2BO_2^- + 2H_3BO_3$$

$$Ba^{++} + 2BO_2^- \rightleftarrows Ba(BO_2)_2$$

$$B_4O_7^{--} + Ba^{++} + 3H_2O \rightleftarrows \downarrow Ba(BO_2)_2 + 2H_3BO_3$$

2. Silver nitrate forms a white precipitate of $AgBO_2$, soluble in HNO_3 and NH_4OH:

$$B_4O_7^{--} + 2Ag^+ + 3H_2O = \downarrow 2AgBO_2 + 2H_3BO_3$$

3. Turmeric Paper Test*. Moisten a piece of turmeric paper with acidified borate solution and dry it. The paper turns brownish red.

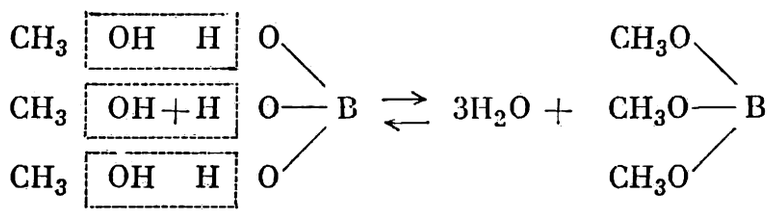
* Turmeric paper consists of strips of ashless filter paper impregnated with turmeric extract and dried in air in a dark place.

Alkalies change the colour to greenish black or (if the solutions are very dilute) violet. This is a highly characteristic test.

4. Flame Test. Volatile boron compounds colour the burner flame green. As borates are non-volatile, the test is carried out by one of the following methods.

(a) Mix a small amount of a solid boron compound, such as $Na_2B_4O_7 \cdot 10H_2O$, on a watch glass or crucible lid with powdered CaF_2 and moisten with a few drops of concentrated H_2SO_4. The boron compound formed (BF_3) is so volatile that if a small amount of the mixture on a glass rod is brought near (*not touching*) the flame, the edge of the flame is coloured green after a little while.

(b) Evaporate $Na_2B_4O_7$ solution* to dryness in a crucible, add about 1 ml of concentrated H_2SO_4 followed by 1-2 ml (not more) of an alcohol, preferably methyl, and put a light to the mixture. The alcohol burns with a characteristic green-edged flame. This reaction is explained as follows. Alcohols are derivatives of hydrocarbons, formed by replacement of hydrogen atoms by hydroxyl groups. For example, methyl alcohol is the hydroxyl derivative of the hydrocarbon methane, CH_4, and has the formula CH_3OH. Ordinary alcohol (ethyl alcohol), C_2H_5OH, is the corresponding derivative of the hydrocarbon ethane, C_2H_6, etc. One characteristic reaction of alcohols is formation of esters with acids. These compounds can be regarded as products formed by replacement of acidic hydrogen atoms by CH_3, C_2H_5, and similar hydrocarbon "radicals". In the present instance the methyl borate ester $B(OCH_3)_3$ is formed; being a very volatile compound of boron, it confers the characteristic colour to the flame. The reaction can be represented as follows:



94. Reactions of Fluoride, F^-

The F^- ion is the anion of hydrofluoric acid HF, which is a volatile liquid boiling at 19.4°. Its vapour has a pungent smell and is *highly poisonous.* In distinction from the other halide acids, HF is an acid of moderate strength. Its characteristic feature is that F^- ions cannot be oxidized by chemical reagents to free F_2,

* As free H_3BO_3 is volatile in steam, acid borate solutions should not be evaporated. Such solutions must first be made alkaline by addition of NaOH.

because the latter is the most powerful oxidizing agent known. Another distinction is that silver fluoride, AgF, is readily soluble in water whereas AgCl, AgBr and AgI are practically insoluble.

Fluorides of the alkali metals, ammonium, aluminium, tin and mercury are soluble in water. Fluorides of alkaline-earth metals, lead, copper, and zinc are practically insoluble.

Fluorides are almost neutral in aqueous solution. The F^- ion is colourless.

1. **Barium chloride** forms a bulky white precipitate of BaF_2, soluble in excess mineral acid and in ammonium salts, with the F^- ion.

2. **Calcium chloride** forms a white precipitate, soluble with difficulty in mineral acids and insoluble in acetic acid.

3. **Silver nitrate** does not form a precipitate with the F^- ion.

4. **Formation of SiF_4.** A characteristic peculiarity of HF is its reaction with SiO_2 and silicates to form gaseous silicon fluoride, SiF_4.

Put a small amount of a solid fluoride (e.g., CaF_2) in a *dry* test tube and treat it with a few drops of concentrated H_2SO_4. Hold a drop of water in a wire loop inside the test tube for some time. The water in the drop becomes turbid owing to formation of a precipitate of silicic acid.

Fluoride reacts with H_2SO_4 as follows:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF \uparrow$$

The hydrogen fluoride formed acts on the silicates of the walls of the test tube to form gaseous silicon fluoride, SiF_4. The composition of ordinary glass roughly corresponds to the formula $Na_2SiO_3 \cdot CaSiO_3 \cdot 4SiO_2$; therefore the reaction may be represented by the equation*

$$SiO_2 + 4HF = SiF_4 \uparrow + 2H_2O$$

Finally, the SiF_4 reacts with the water in the wire loop to form a gel of orthosilicic acid, H_4SiO_4:

$$SiF_4 + 4H_2O = \downarrow H_4SiO_4 + 4HF$$

The turbidity of the drop is due to the formation of orthosilicic acid. This is the most characteristic test for the F^- ion.

To detect F^- by this method in a solution, the latter should first be evaporated to dryness. Alternatively, F^- can first be precipi-

---

* In addition to SiF_4, the fluosilicates of sodium and calcium, Na_2SiF_6 and $CaSiF_6$, are also formed.

tated by addition of $CaCl_2$ in the presence of CH_3COOH, the CaF_2 precipitate filtered off, *dried thoroughly*, and tested for F^- as described above.

5. **Spot Test.** When a drop of alizarin solution is mixed with a drop of a solution of a zirconium salt, such as zirconyl nitrate $ZrO(NO_3)_2$, a violet precipitate of zirconium alizarin lake is formed.

If a small amount of fluoride is then added to the mixture, the zirconium ions form a more stable complex, $[ZrF_6]^{--}$. The violet colour of the zirconium alizarin lake is replaced by the greenish yellow colour of alizarin*.

The reaction can be represented schematically as follows:

$$\underset{\text{(Violet lake)}}{\text{Zr-alizarin}} + 6F^- \rightleftarrows [ZrF_6]^{--} + \underset{\text{(Greenish yellow)}}{\text{alizarin}}$$

Phosphates and oxalates interfere.

6. **Microcrystalloscopic Test.** To a drop of the solution acidified with HCl add a small amount of solid silicic acid followed by

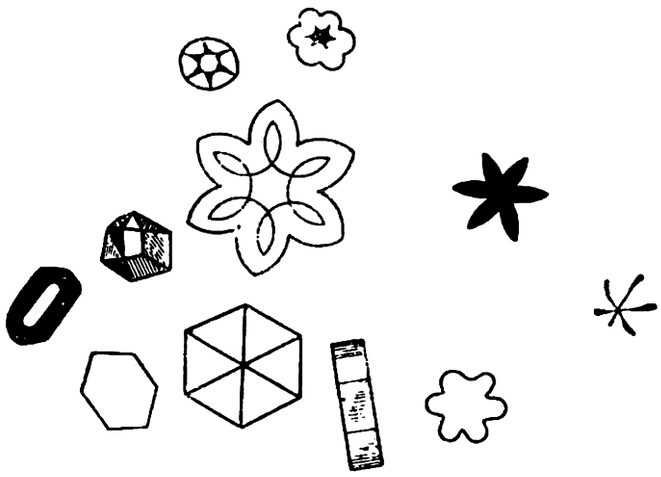


Fig. 44. Crystals of $Na_2[SiF_6]$

a grain of NaCl. Crystals of sodium fluosilicate, Na_2SiF_6, are formed (Fig. 44), sometimes coloured pale pink. The detectable minimum is 0.4 μg F^-. The dilution limit is 1 : 2,500.

95. Reactions of Silicate, SiO_3^{--}

A great variety of silicon compounds, known as silicates, exists in nature; some can be prepared artificially. They are salts of various silicic acids: metasilicic acid H_2SiO_3, orthosilicic acid H_4SiO_4, and polysilicic acids such as $H_4Si_3O_8$, $H_2Si_2O_5$, $H_2Si_3O_7$, etc. Their composition may be represented by the general formula $mSiO_2 \cdot nH_2O$.

* The formula of alizarin is given on p. 267.

In the great majority of cases silicic acids cannot be isolated in the pure state; their existence must be inferred from the existence of the corresponding salts. The only soluble silicates are the alkali metasilicates, Na_2SiO_3 and K_2SiO_3, which are known as "water glasses". Aqueous 0.1 *N* solutions of these compounds are strongly alkaline (pH $>$ 12) owing to hydrolysis. Some insoluble silicates are decomposed by mineral acids to form free silicic acids; others are not. Insoluble silicates which are not decomposed by acids can be brought into solution by fusion with a mixture of Na_2CO_3 and K_2CO_3, soluble alkali silicates being formed in the process.

Silicate solutions are colourless.

1. **Barium chloride** gives a white precipitate of $BaSiO_3$ with SiO_3^{--}. Acids decompose this precipitate to form a gelatinous mixture of various silicic acids.

2. **Silver nitrate** forms a yellow precipitate of Ag_2SiO_3, soluble in HNO_3, with silicate solutions:

$$SiO_3^{--} + 2Ag^+ = \downarrow Ag_2SiO_3$$

3. **Dilute acids**, when added slowly to not very dilute silicate solutions, form a white gelatinous precipitate (gel) consisting of silicic acids. Sometimes the whole mixture in the test tube is converted into a gel. When excess acid is added rapidly, especially to dilute silicate solutions, the precipitate does not form immediately and may not appear for a very long time. Silicic acids then remain in the form of a colloidal solution (sol). A colloidal solution is also partially formed during gel formation. Therefore the precipitation of silicic acids by other acids may be incomplete.

To separate silicic acids completely, the solution is evaporated to dryness several times with concentrated HCl. This renders the silicic acids insoluble and they can be separated by filtration after treatment of the residue with acidified water.

4. **Ammonium salts** precipitate silicic acid from silicate solutions more completely than do acids. The reaction occurs because the silicate hydrolysis equilibrium is disturbed by removal of OH^- ions by NH_4^+ ions from the ammonium salt:

$$\begin{gathered} SiO_3^{--} + 2H_2O = H_2SiO_3 + 2OH^- \\ 2OH^- + 2NH_4^+ = 2NH_4OH \\ \hline SiO_3^{--} + 2H_2O + 2NH_4^+ = \downarrow H_2SiO_3 + 2NH_4OH \end{gathered}$$

If the precipitate does not form in the cold, the solution is heated for several minutes on a water bath.

It must be remembered that when aluminates are heated with NH_4Cl they form a precipitate of $Al(OH)_3$, very similar in appearance

to silicic acids (see p. 264). In the same way, NH_4Cl precipitates hydroxides from the corresponding compounds of tin and antimony. Therefore it is advisable to carry out a confirmatory test for SiO_3^{--}. Evaporate a portion of the solution to dryness, transfer the dry residue to a filter, and treat it with a 0.5 solution of the dye methylene blue in acetic acid. Wash the residue with cold water; if silicate was present, a gelatinous precipitate of silicic acid coloured blue by the dye remains on the filter.

5. **Microcrystalloscopic Test.** Dissolve a small grain of the substance in hydrofluoric acid (or treat it with a solution of NH_4F in HCl) on a glass slide coated with paraffin wax (or on photographic film with the emulsion removed). Put a small crystal of NaCl into the solution. Crystals of $Na_2[SiF_6]$ (see Fig. 44) are formed in the presence of silicon. The detectable minimum is 0.05 μg Si. The dilution limit is 1 : 20,000.

96. Reactions of Oxalate, $C_2O_4^{--}$

The oxalate ion is the anion of oxalic acid, $H_2C_2O_4$; its structural formula is

$$\begin{array}{l} HO-C=O \\ \quad\quad | \\ HO-C=O \end{array}$$

Free oxalic acid is a white substance crystallizing with two molecules of water. It is readily soluble in water, and is a dibasic acid of moderate strength. It sublimes readily on moderate heating. Strong heating decomposes it into H_2O, CO_2 and CO. The only soluble salts of $H_2C_2O_4$ (oxalates) are those of the alkali metals and magnesium. The others are sparingly soluble in water but dissolve in mineral acids.

Oxalic acid forms complex anions with the cations Cr^{+++}, Fe^{+++} and Ni^{++}, and with certain other ions such as $[Cr(C_2O_4)_3]^{---}$, $[Fe(C_2O_4)_3]^{---}$, $[Ni(C_2O_4)_3]^{==}$, etc.

The $C_2O_4^{--}$ anion is colourless.

1. **Barium chloride** forms a white precipitate of BaC_2O_4, soluble in mineral acids and (on boiling) in acetic acid, with $C_2O_4^{--}$.

2. **Silver nitrate** gives a white curdy precipitate of $Ag_2C_2O_4$, soluble in HNO_3 and NH_4OH.

3. **Calcium salts (the Ca^{++} ion)** precipitate the $C_2O_4^{--}$ ion in the form of white CaC_2O_4, soluble in mineral acids but *insoluble in acetic acid.* The action of acetic acid distinguishes CaC_2O_4 from the calcium salts of all other anions studied, with the exception of CaF_2 (and $CaSO_4$, which may be formed at high SO_4^{--} concentrations).

4. Potassium permanganate, $KMnO_4$, *in acid solution* oxidizes $C_2O_4^{--}$ to CO_2:

$$2MnO_4^- + 5C_2O_4^{--} + 16H^+ = 2Mn^{++} + 8H_2O + 10CO_2 \uparrow$$

The solution is heated to 70-80°. The occurrence of the reaction can be easily seen by decolourization of permanganate added drop by drop to the heated acid solution. The decolourization is usually delayed. Addition of 1-2 drops of $MnSO_4$ solution accelerates the reaction catalytically (p. 338). As other reducing agents, such as sulphides, sulphites, thiosulphates and nitrites can decolourize (reduce) $KMnO_4$, the $C_2O_4^{--}$ ion must be separated from other reducing agents by precipitation with $CaCl_2$ in the presence of CH_3COOH before the test.

Proceed as follows. Take a few millilitres of the solution in a test tube and make it *slightly* alkaline with NaOH, in order to neutralize any strong acids which might prevent precipitation of CaC_2O_4. Now add acetic acid to pH = 4-5. Add excess $CaCl_2$ solution and heat for several minutes. Centrifuge off the precipitated calcium salts, wash them *thoroughly* with hot water (to remove residual solution, which may contain reducing agents), and treat with 2 *N* H_2SO_4 on heating. Filter off the residue, add one drop of $MnSO_4$ to the filtrate, heat on the water bath, and add 0.01 *N* permanganate solution drop by drop. Fading of the colour indicates the presence of $C_2O_4^{--}$. In alkaline solution the oxidation of $C_2O_4^{--}$ by permanganate is very slow, so that a negative result in the reaction does not necessarily prove the absence of $C_2O_4^{--}$.

5. Concentrated sulphuric acid abstracts water from oxalic acid on heating, with evolution of equal volumes of CO_2 and CO. The atter burns with a blue flame when lit. The equation is

$$H_2C_2O_4 = H_2O + CO_2 \uparrow + CO \uparrow$$

6. Resorcinol, $C_6H_4(OH)_2$, dissolved in 100 times its own weight of concentrated H_2SO_4, gives a characteristic blue colour when heated with dry oxalates until SO_3 fumes appear.

7. Strong heating decomposes oxalates, with slight charring. Oxalates of the alkali metals and barium form the carbonates and carbon monoxide, e.g.,

$$Na_2C_2O_4 = Na_2CO_3 + CO \uparrow$$

Oxalates of iron, nickel, cobalt, copper and the noble metals are decomposed on heating to leave the free metals, and all other oxalates are decomposed to the oxides.

As oxalates can form complexes with a number of cations, which can therefore be missed in the course of analysis, they must be removed from the substance before analysis for cations. This is done either

by heating the solid substance in air, or by treatment with a mixture of concentrated sulphuric and nitric acids until SO_3 fumes appear; this procedure is repeated several times, until the residue gives a negative test for $C_2O_4^{--}$. Obviously, Ba^{++}, Sr^{++}, Pb^{++} and partially Ca^{++} are converted into sparingly soluble sulphates by this treatment; they are dissolved and analyzed as described earlier.

SECOND GROUP OF ANIONS

Anions of Group II include Cl^- (chloride), Br^- (bromide), I^- (iodide), S^{--} (sulphide), CNS^- (thiocyanate), $[F(CN)_6]^{==}$ (ferrocyanide), $[Fe(CN)_6]^{---}$ (ferricyanide), and some others. *These ions are precipitated by* Ag^+ *ions in nitric acid solution, because their silver salts are insoluble* in dilute* HNO_3.

In contrast to Group II anions, silver salts of Group III anions and of SO_4^{--} and F^- are soluble in water, and silver salts of the remaining Group I anions are soluble in dilute HNO_3.

Therefore *the reagent for anion Group II is* $AgNO_3$ *in the presence of dilute* HNO_3.

Nitric acid oxidizes S^{--} ions to sulphur (or even to SO_4^{--}); therefore in using the group reagent in testing for the presence of Group II anions nitric acid should be added to the silver nitrate solution and not to the unknown solution.

Barium salts of Group II anions are soluble in water. Therefore, unlike Group I anions, *Group II anions are not precipitated by* $BaCl_2$. Group II anions are colourless (with the exception of $[Fe(CN)_6]^{==}$ and $[Fe(CN)_6]^{---}$) in aqueous solution.

97. Reactions of Chloride, Cl^-

The chloride ion is the anion of hydrochloric acid, HCl. This acid is a solution of hydrogen chloride gas in water, and is one of the strongest mineral acids. Chlorides formed from HCl and strong bases, such as NaCl, $CaCl_2$, etc., are therefore neutral in solution while solutions of salts of HCl with weak bases are acidic. This also applies equally to bromides and iodides, because HBr and HI are acids equal in strength to HCl.

Chlorides which are sparingly soluble in water are AgCl, Hg_2Cl_2, $PbCl_2$, and the basic chlorides of bismuth, antimony and tin. All other chlorides are readily soluble.

1. **Silver nitrate** gives a white curdy precipitate of AgCl with the Cl^- ion. The precipitate turns grey-violet and then black on exposure to light (owing to decomposition).

---

* Silver sulphide, Ag_2S, dissolves in HNO_3 on heating.

Being an insoluble salt of a strong acid, AgCl does not dissolve in acids such as HNO_3; however, it is readily dissolved by substances capable of forming complexes with the Ag^+ ion, such as NH_4OH, $Na_2S_2O_3$ or KCN. In the case of NH_4OH the reaction is

$$AgCl + 2NH_4OH = [Ag(NH_3)_2]^+ + Cl^- + 2H_2O$$

When the solution is acidified, AgCl is reprecipitated (Sec. 66):

$$[Ag(NH_3)_2]^+ + Cl^- + 2H^+ = \downarrow AgCl + 2NH_4^+$$

The solubility product of AgI (1.5×10^{-16}) is much lower than that of AgCl (1.6×10^{-10}), and AgI is therefore almost insoluble in ammonia. The solubility of AgBr ($SP = 7.7 \times 10^{-13}$) and AgCNS ($SP = 1.16 \times 10^{-12}$) in ammonia is slight. Even this very low solubility of silver bromide and thiocyanate can be depressed to negligible values by the use of 12% ammonium carbonate solution* as the reagent; this solution, as the result of hydrolysis, is an ammonium buffer mixture of pH $\approx$ 9.2 (p. 131).

When the precipitated silver salts are shaken vigorously with this solution, the chloride dissolves while silver bromide and thiocyanate remain almost unaffected. If the residue is filtered off and a few drops of KBr solution are added to the clear filtrate, in the presence of Cl^- in the original solution the Ag^+ ion concentration in the ammoniacal solution will be high enough to exceed considerably the solubility product of AgBr. Therefore abundant yellowish white turbidity due to AgBr appears in the liquid. Its formation is a sign of the presence of Cl^-. In the absence of chloride the solution remains almost transparent (more correctly, a slight turbidity appears**) because of the very low solubility of silver bromide and thiocyanate in ammonium carbonate.

A special mixture containing 0.25 *M* NH_4OH, 0.25 *M* KNO_3 and 0.01 *M* $AgNO_3$ per litre can also be used for dissolving AgCl. This mixture contains $[Ag(NH_3)_2]^+$ ions, which are formed when silver halides are dissolved in ammonia, e. g.,

$$AgBr + 2NH_4OH \rightleftarrows [Ag(NH_3)_2]^+ + Br^- + 2H_2O$$

in addition to NH_4OH. These ions therefore lower the solubility of silver halides, i. e., they shift the reaction equilibrium to the left. This mixture is a fairly good solvent for AgCl but AgBr is almost

---

* The $(NH_4)_2CO_3$ solution used for precipitation of Group II cations cannot be used for this purpose, because it contains added ammonia.

** To make sure that the results of this test are interpreted correctly, it should be carried out with (a) a mixture of AgCl, AgBr and AgCNS and (b) a mixture of AgBr and AgCNS (without AgCl), the intensity of the turbidity in the two cases being compared.

insoluble in it. Therefore, when a mixture of AgCl, AgBr and AgI is treated with it, only AgCl is dissolved; when the residue has been filtered off, AgCl can be detected in the filtrate by acidification with HNO_3. If AgCNS is present in the precipitate, it is preferable to use $(NH_4)_2CO_3$ as the solvent for detection of Cl^-.

2. **Concentrated H_2SO_4** liberates gaseous HCl from dry chlorides such as NaCl or KCl (HCl can be detected by its odour, and by reddening of blue litmus paper held in the mouth of the test tube). The equation is

$$NaCl + H_2SO_4 = NaHSO_4 + HCl\uparrow$$

3. **Action of Oxidizing Agents.** The high standard oxidation potential (+1.36 V) of the $Cl_2/2Cl^-$ couple shows that free Cl_2 is a very powerful oxidizing agent and the Cl^- ion is a weak reducing agent. However, oxidizing agents with even higher oxidation potentials oxidize Cl^- ions to Cl_2.

Such oxidizing agents include $KMnO_4$, PbO_2 and $KClO_3$ in acid solution. It is sometimes possible to oxidize Cl^- ions by oxidizing agents of lower oxidation potentials if the concentrations of the reacting substances are suitably chosen. For example, if we add a few drops of concentrated H_2SO_4 and a small amount of solid MnO_2 ($E_0 = +1.24$ V) to a chloride solution and heat, Cl_2 is liberated (detected by its smell and by the formation of a blue colour on starch-iodide paper* held in the mouth of the test tube). The equation is

$$MnO_2 + 2Cl^- + 4H^+ \rightleftarrows Cl_2\uparrow + Mn^{++} + 2H_2O$$

The reaction proceeds in this direction because of the high H^+ ion concentration, which greatly raises the oxidation potential of the MnO_2/Mn^{++} couple. Confirm by writing the Nernst equation for this couple.

Since the oxidation potentials of the couples $Br_2/2Br^-$ (+1.07 V) and $I_2/2I^-$ (+0.54 V) are lower than that of $Cl_2/2Cl^-$, it follows that *all oxidizing agents which oxidize* Cl^- *ions to* Cl_2 *must oxidize* I^- *and* Br^- *even more vigorously* to free I_2 and Br_2. It must be noted that, being one of the weakest reducing agents, the Cl^- anion cannot reduce $KMnO_4$ to $MnO(OH)_2$ in alkaline solution.

4. **Reaction with Potassium Dichromate, $K_2Cr_2O_7$, and Sulphuric Acid.** Grind a small amount of a solid chloride, such as NaCl, in a mortar with roughly three times the amount of $K_2Cr_2O_7$ and put the finely powdered mixture in a dry test tube fitted with a gas outlet tube (Fig. 45). Add a small amount of concentrated H_2SO_4, plug the test tube, and insert the end of the gas outlet tube into another test

* Filter paper impregnated with starch and potassium iodide solutions. When KI reacts with Cl_2, free iodine is formed, giving a blue colour with starch.

tube containing 1-2 ml of dilute ammonia. *The end of the tube should not be immersed in the ammonia solution, as this may be sucked into the test tube with sulphuric acid and an explosion could follow.* Warm the test tube with the reaction mixture gently, *watching all the time that the gas outlet tube is in the correct position.* The following reactions take place.

(a) The action of $K_2Cr_2O_7$ on the chloride in the presence of H_2SO_4 gives a volatile chromium compound known as chromyl chloride, CrO_2Cl_2:

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 = 2CrO_2Cl_2 \uparrow + K_2SO_4 + 2Na_2SO_4 + 3H_2O$$

(b) The CrO_2Cl_2 reacts with the ammonia solution in the second test tube to form a chromate:

$$CrO_2Cl_2 + 4NH_4OH = (NH_4)_2CrO_4 + 2NH_4Cl + 2H_2O$$

At the end of the reaction, test for chromate by the perchromic acid (H_2CrO_6) reaction with the solution acidified with H_2SO_4 (see p. 274).

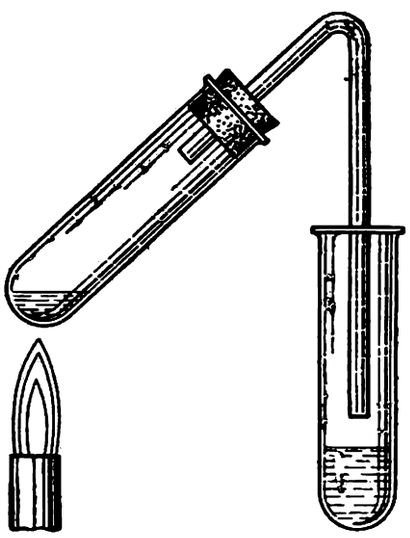


Fig. 45. Detection of Cl^- ions by the reaction with $K_2Cr_2O_7$ and H_2SO_4

Alternatively, take a drop of the solution in a wire loop, transfer it to a test tube with 2-3 drops of 2 *N* CH_3COOH solution, and add a drop of $BaCl_2$ solution. Formation of a yellow precipitate (or turbidity) of $BaCrO_4$ indicates the presence of CrO_4^{--}.

In the absence of fluorides, chromium can be volatilized only in the form of CrO_2Cl_2; therefore the presence of CrO_4^{--} ions in the drop of solution shows that the original substance contained chlorides (Cl^- ions).

Under the same conditions fluorides form liquid (but volatile) chromyl fluoride CrO_2F_2, and therefore interfere. On the other hand, Br^- and I^- do not interfere with the reaction.

This test must be carried out *very carefully*, because if $K_2Cr_2O_7$ enters the drop of liquid from the reaction mixture or from the tube walls the Cl^- ion will be wrongly detected*. This test, together with that outlined in 1, is used for detection of Cl^- in the presence of Br^- and I^-.

---

* This may occur if the test tube with the reaction mixture is heated without due care.

98. Reactions of Bromide, Br^-

The Br^- ion is the anion of hydrobromic acid, HBr which, like HCl, is a solution of hydrogen bromide in water. HBr is an acid of equal strength to HCl. The only salts of hydrobromic acid (bromides) insoluble in water are AgBr, Hg_2Br_2 and $PbBr_2$ (analogy with chlorides). In general, bromides are very similar to chlorides in properties; the main difference is that they are somewhat less resistant to the action of oxidizing agents.

1. Silver nitrate forms a yellowish precipitate of AgBr, insoluble in HNO_3, with solutions of bromides. As was shown earlier, this precipitate is slightly soluble in NH_4OH and almost insoluble in ammoniacal $AgNO_3$ solution. Silver bromide is readily decomposed by the action of zinc dust in the presence of water or 2 *N* H_2SO_4. The following reaction takes place*:

$$2AgBr + Zn = Zn^{++} + 2Br^- + \downarrow 2Ag$$

Silver separates out as a black precipitate, and Br^- ions go into solution and can be detected there.

2. Concentrated H_2SO_4 acts on solid bromides, such as NaBr, to form hydrogen bromide gas:

$$NaBr + H_2SO_4 = NaHSO_4 + HBr \uparrow$$

In distinction from HCl, hydrogen bromide is partially oxidized by sulphuric acid to free Br_2, which colours the liberated gas brownish.

The equation for the reaction is

$$2HBr + H_2SO_4 = Br_2 \uparrow + 2H_2O + SO_2 \uparrow$$

3. Action of Oxidizing Agents. It has already been stated that, because the standard oxidation potential of the $Br_2/2Br^-$ couple ($E_0 = +1.07$ V) is lower than that of $Cl_2/2Cl^-$ ($E_0 = +1.36$ V), the Br^- ion is a stronger reducing agent, i.e., is oxidized more easily, than the Cl^- ion. Therefore all oxidizing agents like $KMnO_4$, $KClO_3$, PbO_2, MnO_2, etc., which oxidize (in acid solution) Cl^- ions to Cl_2 must oxidize Br^- to Br_2 even more readily. However, there are also oxidizing agents which can oxidize Br^- but not Cl^- ions. We had an example of such oxidation in the reaction with concentrated H_2SO_4.

Another example of this kind is the action of chlorine water (solution of Cl_2) or sodium hypochlorite (NaClO) on bromide solu-

---

* *Free bromine is very poisonous; therefore all reactions in which it is formed must be carried out in the fume cupboard.*

tions. Take a small amount of NaBr solution in a test tube, acidify with 2 *N* H_2SO_4, and add chlorine water or NaClO solution drop by drop. The solution turns brown owing to evolution of free Br_2. If we add some benzene* (C_6H_6), which is a better solvent for Br_2 than water, and shake the liquid, the benzene layer acquires a characteristic reddish brown colour due to bromine. In the presence of excess chlorine water the colour changes to yellowish owing to formation of BrCl. This is one of the most important reactions of the Br^- ion.

Being a very weak reducing agent like Cl^-, the Br^- anion cannot reduce $KMnO_4$ to $MnO(OH)_2$ in alkaline solution.

4. Reaction with Fuchsin. The organic dye fuchsin forms a colourless compound with $NaHSO_3$. The action of free bromine on this compound produces a new bromine-substituted dye with a bright reddish violet colour. As free chlorine and iodine do not produce a colour, this test can be used for detecting even very small amounts of Br^- in the presence of Cl^- and I^-.

The test is performed as follows.

Put a few drops of 0.1% aqueous fuchsin solution in a test tube and decolourize the dye by adding solid $NaHSO_3$ and 1 or 2 drops of concentrated HCl. Moisten a piece of filter paper with this solution and attach it to the dry inner surface of the upper watch glass of a gas chamber (see Fig. 10, p. 96). Put 2 or 3 drops of the solution to be tested for Br^- and 4-5 drops of 25% chromic acid solution on the bottom glass, cover it with the top glass, and heat for about 10 minutes over a boiling water bath. The free Br_2 formed by oxidation of Br^- ions by chromic acid reacts more or less rapidly (dependent on the amount of Br^-) with the fuchsin bisulphite compound and colours the paper red-violet. The test is very sensitive**.

99. Reactions of Iodide, I^-

The I^- ion is the anion of hydriodic acid, HI, which is a solution of hydrogen iodide in water. It is an acid of equal strength to HCl and HBr. The iodides insoluble in water are those of silver, mercury and lead, and also cuprous iodide, CuI. Free HI and its salts are oxidized even more easily than HBr and bromides, because the standard oxidation potential of the couple $I_2/2I^-$ (+0.54 V) is even lower than that of $Br_2/2Br^-$ (+0.17 V).

---

* The benzene must be free from unsaturated compounds, which decolourize solutions of Br_2. Chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), or carbon disulphide (CS_2) may be used instead.

** Because of the high sensitivity of this reaction, the chemicals used for preparing the substances to be analyzed must be very pure. For example, potassium iodide may contain traces of bromides, not detectable by other tests, which give an appreciable colouration with this test.

1. **Silver nitrate** forms a yellow precipitate of AgI with I^- ions; this is insoluble in nitric acid and in ammonia (distinction from AgCl). Silver iodide dissolves in $Na_2S_2O_3$ and KCN, which form the complex ions $[Ag(S_2O_3)]^-$, $[Ag_2(S_2O_3)_3]^{==}$ and $[Ag(CN)_2]^-$ with the Ag^+ ion; these complexes are less dissociated than $[Ag(NH_3)_2]^+$. The reaction with $Na_2S_2O_3$ requires a large excess of the latter. The equation is

$$2AgI + 3Na_2S_2O_3 = Na_4[Ag_2(S_2O_3)_3] + 2NaI$$

AgI is also decomposed by zinc in the presence of 2 *N* H_2SO_4:

$$2AgI + Zn + H_2SO_4 = \downarrow 2Ag + ZnSO_4 + 2HI$$

2. **Lead salts** form a golden yellow precipitate of PbI_2 with I^- (Sec. 68).

3. **Concentrated H_2SO_4** has the same effect on iodides as on bromides except that the HI is oxidized to free I_2 even more readily than HBr is oxidized to Br_2. Sulphuric acid is reduced at the same time to SO_2 or H_2S:

$$8HI + H_2SO_4 = 4H_2O + H_2S\uparrow + 4I_2$$

The iodine separates out as a dark grey precipitate or colours the solution brown. If the test tube is heated, violet iodine vapour appears.

4. **Action of Chlorine and NaClO.** Many other oxidizing agents, such as H_2O_2, $KMnO_4$ and $K_2Cr_2O_7$ in acid solution, free Cl_2 and Br_2, NaClO and NaBrO, ferric salts, etc., oxidize iodides in the same way as H_2SO_4. Chlorine water or sodium hypochlorite solution are the reagents most commonly used for detecting I^-, as both I^- and Br^- ions can be found simultaneously by this test.

Mix 2 or 3 drops (not more) of KI and KBr solutions, dilute with 1-2 ml of water, and acidify with sulphuric acid. Add 1-2 ml of benzene* and then chlorine water or NaClO solution drop by drop, shaking the liquid thoroughly after each drop has been added.

As stated in Sec. 62, the I^- ion must be oxidized first, being the stronger of the two reducing agents present. This reaction is represented by the equation

$$2I^- + Cl_2 = I_2 + 2Cl^-$$

and is accompanied by the appearance of a violet colour in the benzene layer, characteristic of I_2. On further addition of chlorine water the colour disappears owing to oxidation of I_2 to iodic acid, HIO_3:

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl$$

---

* See footnote on p. 452.

In the presence of Br^- after the violet colour due to I_2 has disappeared a reddish brown colour due to Br_2 appears, and then changes to the yellow colour of BrCl.

In carrying out this test, take *a very small amount* of the solution to be tested for I^- and Br^-, and add chlorine water or NaClO solution *by single drops*. Otherwise a very large amount of chlorine water may be needed to oxidize all the iodine, and there is a risk of "missing" Br^-; or the colour due to I_2 may disappear instantly and I^- will then be missed.

If the solution also contains the anions S^{--}, $S_2O_3^{--}$ or SO_3^{--}, which are stronger reducing agents than I^- and Br^-, oxidation of the latter can begin only after S^{--}, $S_2O_3^{--}$ and SO_3^{--} have been completely oxidized. They may be oxidized, for example, by $KMnO_4$ in acid solution.

It is even more convenient to test for I^- and Br^- in the precipitate obtained by precipitation of Group II anions by $AgNO_3$ in the presence of HNO_3 (see p. 455).

5. **Potassium or sodium nitrite** in the presence of H_2SO_4 or HCl oxidizes I^- as follows:

$$2I^- + 2NO_2^- + 4H^+ = I_2 + 2H_2O + 2NO \uparrow$$

The I_2 formed in the reaction appears as a dark grey precipitate or colours the solution brown. Its formation can be detected by means of benzene or starch solution. For the starch test, add the brown solution drop by drop to a few drops of starch solution diluted with 2-3 ml of water. The solution turns an intense blue colour owing to the formation of an adsorption compound of starch with iodine. The colour disappears on heating and returns on cooling.

Unlike I^- ions, Br^- ions are not oxidized by nitrites. This is because the oxidation potential of HNO_2 (+0.98 V) is higher than that of I_2 (+0.54 V) but lower than the potential of Br_2 (+1.07 V). The Fe^{+++} ion ($E_0 = +0.77$ V) behaves similarly with I^- and Br^-.

As free iodine is volatile, I^- ions can be removed from solution by means of this reaction. The solution is acidified with $2\,N$ H_2SO_4, nitrite solution is added, and the liquid is boiled until the brown colour of I_2 disappears. Water must be added as it is lost by evaporation in order to prevent volatilization of HBr.

6. **Copper salts**, such as $CuSO_4$, react with I^- as follows:

$$2Cu^{++} + 4I^- = \downarrow 2CuI + I_2$$

The cuprous iodide formed in the reaction appears as an ivory-coloured precipitate*.

* It might seem at first sight that the direction of this reaction is not consistent with the potentials of the couples $I_2/2I^-$ ($E_0 = +0.54$ V) and Cu^{++}/Cu^+ ($E_0 = +0.17$ V). The cause of the inconsistency is the low solubility of CuI

ANALYSIS OF MIXTURES OF Cl^-, Br^-, AND I^- ANIONS *

If Cl^-, Br^- and I^- are present together, they can be detected most conveniently in the precipitate of silver salts formed in nitric acid solution. Reducing anions ($S_2O_3^{--}$, SO_3^{--}, S^{--}), which interfere in tests for I^- and Br^-, are thereby separated and detection of Cl^- is also easier.

1. **Precipitation of Cl^-, Br^- and I^- Ions.** Add 0.5-1.0 ml of $AgNO_3$ solution and 1-2 ml of 6 *N* HNO_3 to 1-2 ml of the unknown solution, and heat. If the precipitate dissolves completely, Cl^-, Br^- and I^- are absent. *Precipitation must be complete* (confirm this), otherwise Cl^- and even Br^- may remain entirely in solution**.

2. **Dissolving AgCl, and Test for Cl^-.** Wash the precipitate and shake it vigorously for 1 minute with 0.5-1 ml of 12% $(NH_4)_2CO_3$ solution. Part of the AgCl dissolves to form $[Ag(NH_3)_2]Cl$, while AgBr and AgI (together with Ag_2S if this was not dissolved completely when heated with HNO_3) remain in the residue. Filter off and wash the precipitate, and investigate as outlined in 3. Add KBr solution drop by drop to the filtrate***.

If $[Ag(NH_3)_2]Cl$ is present, *intense* turbidity appears (owing to formation of AgBr), indicating the presence of Cl^- in the original solution (p. 448).

3. **Dissolving I^-, Br^- and Cl^- Ions.** Wash the precipitate, and add 0.5-1 ml of water and a small amount of zinc dust****. Stir the contents of the test tube with a glass rod for one minute, filter, and discard the precipitate (excess Zn and metallic silver formed in the reaction).

Investigate the filtrate as described in 4.

4. **Tests for I^- and Br^-.** Acidify a portion of the filtrate with 2 *N* H_2SO_4 and test for I^- and Br^- by the action of chlorine water

---

SP $\approx 1 \times 10^{-12}$), so that the Cu^+ ion concentration is greatly reduced and the oxidation potential of the Cu^{++}/Cu^+ couple is correspondingly raised. This potential becomes higher than that of $I_2/2I^-$, and the reaction therefore proceeds in the direction of oxidation of I^- by Cu^{++} ions.

* The procedure described here for detection of Cl^-, Br^- and I^- is suitable only in the absence of CNS^-, $[Fe(CN)_6]^{==}$ and $[Fe(CN)_6]^{---}$. If these ions may be present, proceed as described in Sec. 104.

** As AgCl and AgBr are more soluble than AgI, the latter is precipitated first, followed by AgBr and finally AgCl (Sec. 27).

*** If the filtrate is turbid, pass it several times through the same filter until clear.

**** If a piece of metallic zinc is used instead of zinc dust, the reaction must be carried out in the presence of 2 *N* H_2SO_4 on heating in order to accelerate the reaction and to remove H_2S which may form i the precipitate Ag_2S is present.

or NaClO solution in the presence of benzene (or $CHCl_3$ and similar solvents)*.

The I^- and Br^- ions can be detected also by the following tests:

(a) I^- by the reaction with KNO_2 in the presence of starch;

(b) Br^- by the fuchsin test after oxidation of Br^- to Br_2 (Sec. 98, 4)**.

100. Reactions of Sulphide, S^{--}

The S^{--} ion is the anion of hydrosulphuric acid which, similarly to the halide acids, is a solution of H_2S in water. Hydrosulphuric acid is one of the weakest acids. Therefore the sulphides of strong bases are strongly alkaline in solution. For example, calculations show that 0.1 *N* Na_2S and K_2S solutions have pH $\approx$ 13.0. The pH of $(NH_4)_2S$ solution of the same concentration is 9.25. Some sulphides of weak bases (Al_2S_3, Cr_2S_3, TiS_2) cannot exist in the presence of water, as they are completely hydrolyzed to form the corresponding hydroxides.

The behaviour of sulphides with water, acids, alkalies, and alkali-metal sulphides is used in the separation of cations into groups, and has been described earlier.

As the standard oxidation potential of the couple S/S^{--} is low ($E_0 = -0.51$ V), the S^{--} ion is a very active reducing agent. It is oxidized to free sulphur, SO_2, or even H_2SO_4. We have already met numerous examples of the reducing action of H_2S.

1. **Silver nitrate** gives a black precipitate of Ag_2S with S^{--} ions. The precipitate is insoluble in NH_4OH, but dissolves in dilute HNO_3 on warming.

2. **Acids**, such as dilute H_2SO_4 and HCl, decompose many sulphides with evolution of gaseous H_2S:

$$Na_2S + H_2SO_4 = Na_2SO_4 + H_2S\uparrow$$

$$FeS + 2HCl = FeCl_2 + H_2S\uparrow$$

Hydrogen sulphide can be identified by its characteristic smell of bad eggs, and by the blackening of paper moistened with a solu-

---

* If a greenish yellow colour appears in the benzene layer after disappearance of the violet colour due to I_2 (or immediately, if I^- is absent), the cause is Cl_2 dissolved in benzene. In such cases carry out a "blank" experiment, taking 3 drops of water instead of the unknown solution, and compare the colours obtained in the two cases.

** When using this highly sensitive test, take into account the footnote on p. 452. If a large amount of I^- is present, it can be removed by boiling with KNO_2 and H_2SO_4 (Sec. 99, 5), and Br^- is then detected by means of chlorine water or NaClO (Sec. 98, 3).

tion of lead acetate, $(CH_3COO)_2Pb$, or of a plumbite such as Na_2PbO_2*, when the paper is held near the mouth of a test tube in which H_2S is evolved:

$$H_2S + (CH_3COO)_2Pb = \downarrow PbS + 2CH_3COOH$$

$$H_2S + Na_2PbO_2 = \downarrow PbS + 2NaOH$$

Sulphides which are not decomposed by acids can be decomposed if they are mixed with zinc dust** and treated with HCl. Hydrogen sulphide, which can be detected as described above, is given off together with hydrogen.

3. **Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$,** reacts with the S^{--} ion (but not with HS^-) to give a characteristic red-violet colour due to the formation of the complex compound $Na_4[Fe(CN)_5NOS]$.

Free hydrosulphuric acid, which gives rise to HS^- ions almost exclusively, does not give a colour with sodium nitroprusside On addition of alkali the colour appears, because a large amount of the S^{--} ions needed for the reaction is formed:

$$H_2S + 2OH^- = S^{--} + 2H_2O$$

4. **Cadmium salts** form a characteristic bright yellow precipitate of CdS with the S^{--} ion. If the precipitate is filtered off and treated with $CuSO_4$ solution, it turns black owing to formation of CuS:

$$CdS + Cu^{++} = Cd^{++} + CuS$$

The formation of CdS is used for separating S^{--} from other anions containing sulphur. However, if soluble cadmium salts were used $CdSO_3$ would be precipitated together with CdS; therefore solid cadmium carbonate, $CdCO_3$, should be used as the reagent. As cadmium carbonate is difficultly soluble in water, it gives a very low concentration of Cd^{++} ions in solution. This concentration is nevertheless quite sufficient to exceed the solubility product of cadmium sulphide, which is less soluble than cadmium carbonate and is therefore completely precipitated:

$$CdCO_3 + S^{--} = \downarrow CdS + CO_3^{--}$$

On the other hand, the solubility product of $CdSO_3$ is not reached and the SO_3^{--} ion remains in solution.

---

* It will be remembered that sodium plumbite is formed by the action of excess NaOH on a solution of a lead salt.

** It must be confirmed by a preliminary experiment that the zinc does not contain sulphide as an impurity, i.e., that it does not evolve H_2S when treated with HCl.

5. Reduction Reactions of the Sulphide Ion. Because of the low standard oxidation potential of the couple S/S^{--} ($E_0 = -0.51$ V), the S^{--} is very readily oxidized to free sulphur and is therefore a strong reducing agent. For example, like SO_3^{--} and $S_2O_3^{--}$, it decolourizes free iodine, reducing it to I^- ions:

$$S^{--} + I_2 = \downarrow S + 2I^-$$

It also reduces $KMnO_4$ in acid or alkaline solutions; in the latter case a brown precipitate of $MnO(OH)_2$ is formed as usual. We have already met a number of other reactions in which various oxidizing agents are reduced by S^{--} ions. For example, they reduce Fe^{+++} to Fe^{++} (p. 276), AsO_4^{---} to AsO_3^{---} (p. 386), etc. The oxidation products of S^{--} ions may be SO_2 or even H_2SO_4 in addition to free sulphur.

ANALYSIS OF MIXTURES OF S^{--}, $S_2O_3^{--}$, SO_3^{--} AND SO_4^{--} ANIONS

Systematic analysis is required for detection of S^{--}, $S_2O_3^{--}$ and SO_3^{--} ions when present together, because some of them interfere in tests for others. For example, if the solution contains S^{--} and SO_3^{--} ions, addition of acid liberates H_2S and SO_2 simultaneously, and the two immediately interact:

$$SO_2 + 2H_2S = \downarrow 3S + 2H_2O$$

As a result of this reaction only the gas present in excess will be detected. If this gas is SO_2, addition of acid would be accompanied by the same effects (formation of SO_2 and S) as would be observed if the solution contained $S_2O_3^{--}$. Thiosulphate would therefore be wrongly found. It is obvious that a mixture of SO_3^{--} and $S_2O_3^{--}$ ions would behave on acidification in the same way as $S_2O_3^{--}$ by itself. Finally, in the presence of S^{--} the test for SO_3^{--} with fuchsin or the nitroprusside test with addition of $ZnSO_4$ and $K_4[Fe(CN)_6]$ (pp. 433-434) cannot be used, etc.

Similarly, the detection of SO_4^{--} is difficult in the presence of $S_2O_3^{--}$ ions or mixtures of S^{--} and SO_3^{--}. In both cases a white precipitate of sulphur is formed when the solution is acidified in the test with $BaCl_2$; because it is insoluble in acids, it may be mistaken for $BaSO_4$.

The systematic analysis of mixtures of S^{--}, $S_2O_3^{--}$, SO_3^{--} and SO_4^{--}, described in detail below, is based on (a) precipitation of S^{--} by the action of $CdCO_3$, when SO_3^{--}, SO_4^{--} and $S_2O_3^{--}$ remain in solution; (b) precipitation of SO_3^{--} and SO_4^{--} by a strontium salt, which does not precipitate $S_2O_3^{--}$; (c) the fact that $SrSO_4$ is almost insoluble while $SrSO_3$ is soluble in dilute acids.

1. Detection and Separation of S^{--}. Add 1 ml of sodium nitroprusside solution to 1 ml of the *alkaline* solution to be tested. A red-violet colour proves the presence of S^{--}. If S^{--} is present, add a small amount of solid $CdCO_3$ to 2-3 ml of the solution and shake*. Filter and test for complete precipitation by adding sodium nitroprusside to the filtrate. Add more $CdCO_3$ if necessary and again shake the test tube. When the precipitation is complete, filter off and wash the precipitate, which contains CdS and other cadmium salts together with excess $CdCO_3$. Yellow colour of the precipitate confirms the presence of S^{--}. If the colour is indistinct, add $CuSO_4$ solution to the test tube and acidify with 2 *N* HCl. The acid dissolves $CdCO_3$ and the yellow CdS precipitate is replaced by the less soluble black CuS**.

The filtrate, which may contain $S_2O_3^{--}$, SO_3^{--} and SO_4^{--} (and other anions) is investigated according to 2 and 3.

2. Test for $S_2O_3^{--}$. Add 2 *N* HCl solution to a portion of the filtrate (or of the original solution if S^{--} is absent) until acid, and heat. White or yellowish turbidity (due to sulphur) indicates the presence of $S_2O_3^{--}$.

3. Tests for SO_3^{--} and SO_4^{--}. To the remainder of the filtrate add $SrCl_2$ or $Sr(NO_3)_2$ solution until precipitation is complete. *Wash* the precipitate ($SrSO_3$, $SrSO_4$ and other strontium salts) *thoroughly* (to remove $S_2O_3^{--}$ ions), suspend it in 1-2 ml of water, and divide the turbid suspension into two parts.

a. Test for SO_3^{--}. To one portion add 2 *N* HCl followed by iodine solution added drop by drop. If the iodine colour fades, SO_3^{--} is present.

b. Test for SO_4^{--}. Treat another portion of the solution with $BaCl_2$ solution (to convert $SrSO_4$ into the less soluble $BaSO_4$) and excess 2 *N* HCl. If the precipitate does not dissolve, SO_4^{--} is present. It can also be detected in a separate portion of the original solution by the action of $BaCl_2$ in the presence of HCl and $KMnO_4$ (see Sec. 88, 1).

101. Reactions of Thiocyanate, CNS^-

The thiocyanate ion is the anion of thiocyanic acid, HCNS. It is a colourless liquid with a sharp smell, and behaves like a strong monobasic acid in aqueous solutions. Most thiocyanates are readily soluble in water. The thiocyanates of silver, copper, mercury (and gold) are insoluble; the lead salt is soluble with difficulty. The CNS^- ion is colourless.

---

* The $CdCO_3$ must be free from sulphate.

** The S^{--} ion can also be identified by liberation of H_2S in a gas chamber when the precipitate is treated with dilute (1:1) HCl.

1. **Silver nitrate** precipitates CNS^- in the form of white silver thiocyanate:

$$Ag^+ + CNS^- = \downarrow AgCNS$$

The precipitate is insoluble in dilute nitric acid and, in accordance with its solubility product (1.16×10^{-12}), which is close to that of AgBr (7.7×10^{-13}), is slightly soluble in NH_4OH. Like AgBr, it is almost insoluble in $(NH_4)_2CO_3$ solution.

2. **Mercuric nitrate, $Hg(NO_3)_2$,** forms a white precipitate of mercuric thiocyanate, soluble in excess to form a complex compound:

$$Hg(NO_3)_2 + 2KCNS = \downarrow Hg(CNS)_2 + 2KNO_3$$

$$Hg(CNS)_2 + 2KCNS = K_2[Hg(CNS)_4]$$

The ionic equation for the reaction is

$$Hg^{++} + 4CNS^- = [Hg(CNS)_4]^{--}$$

3. **Ferric salts** give a red colour (or pink at low CNS^- concentrations) with CNS^- ions owing to formation of ferric thiocyanate*:

$$Fe^{+++} + 3CNS^- \rightleftarrows Fe(CNS)_3$$

The solution should be acidified in order to suppress hydrolysis of $Fe(CNS)_3$, as otherwise the red colour of the solution changes to red-brown or even yellowish (in very dilute solutions).

At low CNS^- concentrations the weak colour can be intensified by extracting ferric thiocyanate in organic solvents, such as amyl alcohol or ether, in which it is more soluble than in water.

This is the most important reaction for detection of CNS^-. However, many substances which form stable complexes with Fe^{+++} interfere. These substances include oxalic, tartaric, citric and acetic acids, PO_4^{---} and F^- ions, and the $[Fe(CN)_6]^{=-}$ ion, which precipitates Fe^{+++} in the form of Prussian blue. Iodide must also be absent, because I^- is oxidized by Fe^{+++} to free I_2 and a brownish red colour similar to that of $Fe(CNS)_3$ appears. To detect CNS^- in the presence of these substances or ions, we must remove $[Fe(CN)_6]^{=-}$ ions from the solution by means of $ZnSO_4$ or $(CH_3COO)_2Zn$ and treat the filtrate with $AgNO_3$ solution in the presence of HNO_3. This precipitates CNS^- ions and thus separates them from most of the interfering substances, which remain in solution. To bring the CNS^- ions back into solution and to separate them from I^- ions, the precipitate (which may contain AgCNS, AgCl, AgBr, AgI and Ag_2S) is shaken with KBr solution. Most of

* This reaction is really more complicated than shown (p. 228). A series of iron thiocyanate complexes is formed ranging from $Fe[CNS]^{++}$ to $[Fe(CNS)_6]^{---}$.

the AgCNS is converted into the less soluble silver bromide and CNS^- ions appear in solution:

$$AgCNS + Br^- = AgBr + CNS^-$$

In contrast to silver thiocyanate, silver iodide is not converted into AgBr to any appreciable extent by the action of KBr (because its solubility product is much lower than that of AgBr), and therefore I^- ions do not go into solution. Therefore CNS^- is separated from I^- and can be detected by addition of $FeCl_3$ to the solution.

Alternatively, a drop of $FeCl_3$ solution may be added to a separate portion of the precipitate on a spot plate. In the presence of CNS^- the precipitate becomes noticeably pink.

4. Action of H_2SO_4. Dilute (1 : 1) H_2SO_4 decomposes dry thiocyanates with evolution of carbonyl sulphide, COS (*poisonous!*), which burns with a blue flame:

$$CNS^- + 2H^+ + H_2O = NH_4^+ + COS$$

Concentrated sulphuric acid decomposes dry thiocyanates rapidly with evolution of various gases and vapours with a sharp smell (COS, HCOOH, CS_2, CO_2, SO_2) and formation of sulphur.

5. Oxidizing agents oxidize the sulphur in CNS^- as follows:

$$S^{-II} - 8e = S^{+VI}$$

Nitric acid, even if dilute, decomposes thiocyanates:

$$3CNS^- + 10H^+ + 13NO_3^- = 16NO\uparrow + 3CO_2\uparrow + 3SO_4^{--} + 5H_2O$$

Permanganate in acid or alkaline (or neutral) solution also oxidizes CNS^-.

The reaction in acid solution is:

$$6MnO_4^- + 5CNS^- + 13H^+ = 6Mn^{++} + 5HCN\uparrow + 5SO_4^{--} + 4H_2O$$

A very small amount (1-2 drops) of thiocyanate solution must be used for this experiment, which must be carried out in a fume cupboard, because the HCN *vapour evolved is extremely poisonous!* To observe the reaction, dilute permanganate solution may be added drop by drop to acidified thiocyanate solution; the permanganate is decolourized.

6. Copper salts (Cu^{++} ions) added drop by drop first produce an emerald-green colour with thiocyanates. A black precipitate of $Cu(CNS)_2$ is formed with an excess of the reagent. In the presence of sulphurous acid, a white precipitate of the cuprous salt $Cu_2(CNS)_2$ is formed instead:

$$2CNS^- + 2Cu^{++} + SO_2 + 2H_2O = \downarrow Cu_2(CNS)_2 + SO_4^{--} + 4H^+$$

7. Cobalt salts (Co^{++} ions) form complex compounds with thiocyanates, soluble in amyl alcohol to give a blue ring (see Sec. 58, 5). A dilute solution of $Co(NO_3)_2$ must be used, added a drop at a time, because the complex $[Co(CNS)_4]^{--}$ is formed only in the presence of a large excess of CNS^- ions.

8. Sodium nitrite, $NaNO_2$, does not react with thiocyanates in neutral solution. When the solution is acidified with mineral acid a dark colour appears, vanishing after some time. The colour is due to oxidation of the CNS^- ion. The course of the reaction is not understood.

9. Metallic zinc in acid solution decomposes thiocyanates (including AgCNS) to form hydrogen sulphide and HCN:

$$Zn + CNS^- + 3H^+ = Zn^{++} + H_2S\uparrow + HCN\uparrow$$

THIS REACTION MUST BE CONDUCTED IN A FUME CUPBOARD.

102. Reactions of Ferrocyanide, $[Fe(CN)_6]^{==}$

The ferrocyanide ion is the anion of ferrocyanic acid, $H_4[Fe(CN)_6]$. This strong acid is a white crystalline solid, readily soluble in water and alcohol. It is stable in the solid state, but gradually turns blue in the presence of moisture as the result of oxidation with formation of Prussian blue. Its salts, the ferrocyanides, are more stable. Only the ferrocyanides of the alkali and alkaline-earth metals are soluble in water*. They form almost neutral solutions. Most of the other ferrocyanides are almost insoluble or very slightly soluble in water and in cold dilute acids. The $[Fe(CN)_6]^{==}$ ion is greenish yellow. Use a solution of $K_4[Fe(CN)_6]$ for studying its reactions.

1. Silver nitrate gives a white precipitate of silver ferrocyanide with the $[Fe(CN)_6]^{==}$ ion, almost insoluble in dilute acetic acid and in ammonia:

$$4Ag^+ + [Fe(CN)_6]^{==} = \downarrow Ag_4[Fe(CN)_6]$$

2. Ferric salts in neutral or slightly acid solutions give a blue precipitate of Prussian blue:

$$4Fe^{+++} + 3[Fe(CN)_6]^{==} = \downarrow Fe_4[Fe(CN)_6]_3$$

The precipitate is soluble in concentrated but not in dilute HCl. It also dissolves in oxalic acid to form the complex compound $H_3[Fe(C_2O_4)_3]$. The presence of CNS^-, which forms blood-red

* The double salt of calcium and ammonium is relatively insoluble; its formation is used in a qualitative test for Ca^{++} (p. 169).

$Fe(CNS)_3$ with Fe^{+++} ions, interferes in this very important reaction of the $[Fe(CN)_6]^{==}$ ion. The interfering effect is easily avoided if the reaction is conducted as a spot test.

Put a drop of saturated lead nitrate solution, a drop of the unknown solution, another drop of $Pb(NO_3)_2$, and a drop of water in that sequence on a strip of filter paper. A precipitate of lead ferrocyanide is formed in the centre of the spot while the CNS^- ions, which are not precipitated by Pb^{++}, are displaced to the edges of the spot and are thus separated from the $[Fe(CN)_6]^{==}$ ions. Now moisten the centre of the spot with $FeCl_3$ solution and dilute HCl. Lead ferrocyanide is converted into Prussian blue and the centre of the spot turns blue.

3. Cupric salts in neutral or acetic acid solutions form a red-brown precipitate of copper ferrocyanide, soluble in mineral acids and in ammonia:

$$2Cu^{++} + [Fe(CN)_6]^{==} = \downarrow Cu_2[Fe(CN)_6]$$

4. Zinc salts give a white precipitate, soluble in alkalies:

$$3Zn^{++} + 2K^+ + 2[Fe(CN)_6]^{==} = \downarrow K_2Zn_3[Fe(CN)_6]_2$$

$$K_2Zn_3[Fe(CN)_6]_2 + 12OH^- = 2K^+ + 2[Fe(CN)_6]^{==} + 3ZnO_2^{--} + 6H_2O$$

5. Ferrous sulphate forms a white precipitate of $Fe_2[Fe(CN)_6]$, which gradually turns blue owing to oxidation to Prussian blue.

6. Sulphuric acid (dilute) does not decompose ferrocyanides in the cold. They are decomposed on boiling with formation of hydrocyanic acid (*strongly poisonous*; *a fume cupboard must be used*):

$$[Fe(CN)_6]^{==} + 6H^+ = Fe^{++} + 6HCN \uparrow$$

Concentrated H_2SO_4 decomposes all ferrocyanides on heating:

$$[Fe(CN)_6]^{==} + 12H^+ + 6H_2O = Fe^{++} + 6NH_4^+ + 6CO \uparrow$$

Sulphuric acid oxidizes Fe^{++} ions and is itself reduced to SO_2:

$$2Fe^{++} + SO_4^{--} + 4H^+ = 2Fe^{+++} + 2H_2O + SO_2 \uparrow$$

7. Caustic alkalies decompose all insoluble ferrocyanides to form ferrocyanides of the alkali metals and the corresponding hydroxides, e.g.,

$$Fe_4[Fe(CN)_6]_3 + 12OH^- = \downarrow 4Fe(OH)_3 + 3[Fe(CN)_6]^{==}$$

$$Cu_2[Fe(CN)_6] + 4OH^- = \downarrow 2Cu(OH)_2 + [Fe(CN)_6]^{==}$$

8. Oxidizing agents, such as potassium permanganate or dichromate, chlorine, bromine, etc., in acid solution oxidize $[Fe(CN)_6]^{==}$ to

$[Fe(CN)_6]^{---}$, e.g.,

$$MnO_4^- + 5[Fe(CN)_6]^{==} + 8H^+ = Mn^{++} + 5[Fe(CN)_6]^{---} + 4H_2O$$

The $KMnO_4$ solution is decolourized. In alkaline solution permanganate is reduced by $[Fe(CN)_6]^{==}$ ions to $MnO(OH)_2$.

103. Reactions of Ferricyanide, $[Fe(CN)_6]^{---}$

The ferricyanide ion is the anion of ferricyanic acid, $H_3[Fe(CN)_6]$. The free acid is a brown crystalline substance, readily soluble in water. It is stable when kept in the dark, but decomposes on exposure to light with formation of hydrocyanic acid, HCN.

Ferricyanic acid is a strong tribasic acid and an oxidizing agent. The ferricyanides of the alkali and alkaline-earth metals, and of ferric iron, chromium (III) and aluminium, are soluble in water. The remaining ferricyanides do not dissolve even in dilute acids. Solutions of ferricyanides are yellowish brown. They are nearly neutral. Use $K_3[Fe(CN)_6]$ solution for the experiments.

1. **Silver nitrate** gives an orange precipitate of silver ferricyanide with the $[Fe(CN)_6]^{---}$ ion:

$$3Ag^+ + [Fe(CN)_6]^{---} = \downarrow Ag_3[Fe(CN)_6]$$

The precipitate is insoluble in nitric acid, but dissolves in ammonia. The action of ammonia distinguishes $Ag_3[Fe(CN)_6]$ from $Ag_4[Fe(CN)_6]$.

2. **Ferrous salts** give a blue precipitate of Turnbull's blue in neutral and acid solutions:

$$3Fe^{++} + 2[Fe(CN)_6]^{---} = \downarrow Fe_3[Fe(CN)_6]_2$$

The difficulty with this very important reaction of the $[Fe(CN)_6]^{---}$ ion is that ferrous salts are easily oxidized in air and therefore usually contain Fe^{+++} ions in addition to Fe^{++}. In the presence of $[Fe(CN)_6]^{==}$ ions, Fe^{+++} gives a precipitate of Prussian blue, indistinguishable in appearance from $Fe_3[Fe(CN)_6]_2$. Therefore the purity of the reagent ($FeSO_4$) must be tested in order that $[Fe(CN)_6]^{---}$ should not be incorrectly reported as present when $[Fe(CN)_6]^{==}$ has been found. The ferrous sulphate must not give a colour with NH_4CNS solution. If the reagent is not pure, the test described below (see 6, *a*) with $MnSO_4$ in the presence of alkali* should be used for detection of $[Fe(CN)_6]^{---}$ ions.

---

* Fe^{+++} ions can be removed from the $FeSO_4$ reagent by boiling with metallic iron, or with reducing agents such as hydrazine or hydroxylamine sulphate, etc. The boiling must be continued until a negative reaction for Fe^{+++} is obtained with NH_4CNS. The treated $FeSO_4$ solution free from Fe^{+++} ions is used immediately for the test for $[Fe(CN)_6]^{---}$.

3. Ferric salts do not give a precipitate, but produce a brown colour (distinction from $[Fe(CN)_6]^{=}$).

4. Zinc salts react with $[Fe(CN)_6]^{---}$ to give a yellow precipitate of $Zn_3[Fe(CN)_6]_2$. This reaction can be used to separate $[Fe(CN)_6]^{---}$ and $[Fe(CN)_6]^{=}$ from CNS^-, Cl^-, Br^- and I^-. The same purpose is achieved with Cd^{++}, which does not precipitate CNS^-, Cl^-, Br^-, and I^- ions.

5. Copper sulphate, $CuSO_4$, gives a green precipitate of $Cu_3[Fe(CN)_6]_2$.

6. Oxidation Reactions. The anion $[Fe(CN)_6]^{---}$, which contains ferric iron, is easily reduced to $[Fe(CN)_6]^{=}$ and is therefore an oxidizing agent. It can oxidize organic substances (oxalic acid, cellulose, sugar) and ammonia as well as such easily oxidized substances as sulphides (S^{--} ions), sulphites (SO_3^{--} ions), etc. Oxidation by ferrocyanides usually proceeds most readily in alkaline solution. Some oxidation reactions are discussed below.

a. Oxidation of Mn^{++} *to* $MnO(OH)_2$. Put a drop of $MnSO_4$ solution and a drop of 2 *N* NaOH on a spot plate. Treat the resultant manganous hydroxide *immediately* with a drop of ferricyanide solution. The precipitate changes colour to dark brown owing to formation of $MnO(OH)_2$:

$$Mn(OH)_2 + 2[Fe(CN)_6]^{---} + 2OH^- = \downarrow MnO(OH)_2 + 2[Fe(CN)_6]^{=} + H_2O$$

As $Mn(OH)_2$ is oxidized by atmospheric oxygen, the reaction mixture gradually turns brown even in the absence of $[Fe(CN)_6]^{---}$. To avoid error, put a drop of $MnSO_4$ and a drop of caustic alkali in a neighbouring depression on the spot and compare the colour of the precipitate in this "blank" experiment with the colour in the test.

This is a very important reaction, because, in addition to the action of Fe^{++}, it can be used for distinguishing $[Fe(CN)_6]^{---}$ from $[Fe(CN)_6]^{=}$. Apart from $[Fe(CN)_6]^{--}$, only the MnO_4^- and CrO_4^{--} ions among the ions considered in this book give this reaction.

b. Oxidation of I^- *ions to* I_2. Acidify some KI solution with sulphuric acid and add a few drops of benzene or chloroform followed by 1-2 drops of ferricyanide solution, and shake. The solvent layer is coloured violet by the liberated iodine:

$$2[Fe(CN)_6]^{---} + 2I^- = 2[Fe(CN)_6]^{=} + I_2$$

Most other oxidizing anions such as MnO_4^-, CrO_4^{--}, NO_2^-, AsO_4^{---}, etc., give this reaction.

c. Benzidine and diphenylamine are oxidized by $[Fe(CN)_6]^{---}$ ions (and by many other oxidizing agents) with formation of a blue precipitate or colour.

7. Caustic alkalies and carbonates (such as Na_2CO_3) decompose all insoluble ferricyanides on boiling; the $[Fe(CN)_6]^{---}$ ion goes into solution and can be detected there:

$$Fe_3[Fe(CN)_6]_2 + 6OH^- = \downarrow 3Fe(OH)_2 + 2[Fe(CN)_6]^{---}$$

104. Analysis of Mixtures of Group II Anions

Individual anions of Group II interfere in tests for other anions in the same group. For example, S^{--} ions (like other reducing agents) interfere with detection of I^- and Br^- by oxidation to the free halogens; $[Fe(CN)_6]^{=}$ and I^- ions interfere with detection of CNS^-; $[Fe(CN)_6]^{---}$ ions interfere with detection of Cl^-. Therefore, if a solution may possibly contain all the Group II anions, the systematic analytical procedure described below should be used. It is based on: (a) separation of S^{--}, $[Fe(CN)_6]^{=}$ and $[Fe(CN)_6]^{---}$ ions by precipitation with Zn^{++}; (b) separation of Cl^-, Br^-, I^- and CNS^- from other anions by precipitation as AgCl, AgBr, AgI and AgCNS in nitric acid solution.

Treatment of the precipitated silver salts with KBr solution dissolves the CNS^- ion, which is then detected in the solution by the test with $FeCl_3$. The Cl^- ion is extracted from the precipitate by treatment with $(NH_4)_2CO_3$ solution and detected by addition of KBr. The I^- and Br^- ions are dissolved out by the action of Zn and H_2SO_4 and detected by the test with chlorine water.

1. Tests for $[Fe(CN)_6]^{=}$ and $[Fe(CN)_6]^{---}$ Ions.

(a) Acidify a portion (1 ml) of the solution with 2 *N* HCl and add $FeCl_3$ solution. A blue precipitate (or colour) due to formation of Prussian blue, $Fe_4[Fe(CN)_6]_3$, indicates the presence of $[Fe(CN)_6]^{=}$. If the presence of CNS^- prevents observation of the colour, test for $[Fe(CN)_6]^{=}$ by the spot test on $Pb(NO_3)_2$ (see Sec. 102, 2).

(b) Acidify another portion (1 ml) of the solution with 2 *N* HCl and add $FeSO_4$ *free from* Fe^{+++}, i.e., not giving a colour with NH_4CNS (*test this*)*. Immediate formation of a blue precipitate of Turnbull's blue, $Fe_3[Fe(CN)_6]_2$, indicates the presence of $[Fe(CN)_6]^{---}$ ions**.

If sufficiently pure $FeSO_4$ is not available, the following test for $[Fe(CN)_6]^{---}$ can be used. Put one drop each of $MnSO_4$ and 2 *N* NaOH solutions on a spot plate, and add 1-2 drops of the solu-

---

* See footnote on page 464.

** If the precipitate is originally white and gradually turns blue, this proves the presence of $[Fe(CN)_6]^{=}$ (the precipitate of $Fe_2[Fe(CN)_6]$ is oxidized to Prussian blue by atmospheric oxygen).

tion to be tested. A brown colour due to formation of $MnO(OH)_2$ indicates* the presence of $[Fe(CN)_6]^{---}$. If the colour does not appear immediately, a "blank" experiment must be carried out (see p. 465).

2. **Test for S^{--}.** Treat 1 ml of the *alkaline* solution with a solution of sodium nitroprusside, $Na_2[Fe(CN)_5NO]$. A red-violet colour indicates the presence of S^{--}. In the absence of SO_3^{--} and $S_2O_3^{--}$ the following test can be used as an alternative. Acidify 2-3 drops of the solution on the lower watch glass of a gas chamber with 2-3 drops of 2 *N* H_2SO_4 or HCl and cover *immediately* with another watch glass to which a piece of paper moistened with $(CH_3COO)_2Pb$ or Na_2PbO_2 solution is attached. Blackening of the paper proves the presence of S^{--}.

If the solution contains SO_3^{--} or $S_2O_3^{--}$, a negative result in this test is inconclusive, because all the hydrogen sulphide evolved may be oxidized by the simultaneously liberated SO_2 to free sulphur:

$$2H_2S + SO_2 = 2H_2O + \downarrow 3S$$

3. **Separation of $[Fe(CN)_6]^{==}$, $[Fe(CN)_6]^{---}$ and S^{--} Ions.** If previous tests have shown the presence of $[Fe(CN)_6]^{==}$, $[Fe(CN)_6]^{---}$ or S^{--} anions, remove them from a portion of the solution. To do this, add $ZnSO_4$ or $(CH_3COO)_2Zn$ solution to the neutral or weakly alkaline solution and heat. Conform complete precipitation, filter, and reject the precipitate (which contains zinc salts of $H_4[Fe(CN)_6]$, $H_3[Fe(CN)_6]$, H_2S, H_2CO_3, H_3PO_4 and other acids); investigate the filtrate, which may contain CNS^-, Cl^-, Br^-, I^-, $S_2O_3^{--}$ and other anions, according to 4.

4. **Precipitation of Cl^-, Br^-, I^- and CNS^-.** Acidify the filtrate from the zinc salts (or 2-3 ml of the original solution if the anions $[Fe(CN)_6]^{==}$, $[Fe(CN)_6]^{---}$ and S^{--} are absent) with 6 *N* HNO_3, heat for several minutes (to oxidize $S_2O_3^{--}$) and add excess $AgNO_3$. *Ensure complete precipitation*, as otherwise certain anions, such as Cl^-, CNS^- or Br^-, may not be precipitated and would be missed (see Sec. 27). Wash the precipitate once and investigate as outlined in 5 and 6. The filtrate is discarded.

5. **Test for CNS^-.** The precipitate may contain AgCl, AgBr, AgI, AgCNS and S (formed as the result of oxidation of $S_2O_3^{--}$ by nitric acid). Suspend it in a few millilitres of water, transfer a small portion of the turbid liquid into another test tube, and shake it with KBr solution. Most of the AgCNS is converted into AgBr and CNS^- ions go into solution. Filter, reject the precipitate, and add $FeCl_3$ solution to the filtrate. A red colour indicates the presence of CNS^-.

---

* The test cannot be used in the presence of MnO_4^- and CrO_4^- ions, which, like $[Fe(CN)_6]^{---}$, can oxidize Mn^{++} to $MnO(OH)_2$.

A separate portion of the precipitate can be treated directly with $FeCl_3$ solution. If it turns pink, CNS^- is present (see p. 461).

6. Test for Cl^-. Shake the remainder of the precipitated silver salts for about a minute with 12% $(NH_4)_2CO_3$ solution (prepared without addition of NH_4OH). Filter off the undissolved residue, wash, and investigate according to 7. Add KBr solution to the filtrate and stir. *Abundant* turbidity due to AgBr indicates the presence of Cl^- in the solution. A very faint turbidity may appear in the absence of chloride (see footnote on p. 448).

7. Tests for I^- and Br^-. Before testing for I^- and Br^-, bring them into solution by the action of zinc and sulphuric acid. If the precipitate contains AgCNS, it forms H_2S and the *extremely poisonous* hydrocyanic acid, HCN, during this reaction. The hydrocyanic acid is given off in the form of vapour; therefore *the operation must be performed in an efficient fume cupboard.* Treat the precipitate in the fume cupboard with H_2SO_4, add a small amount of zinc dust, and heat on a water bath until evolution of gases (H_2, H_2S, HCN) stops completely. Heat the contents of the test tube for a few more minutes, confirm by means of a piece of paper moistened with $(CH_3COO)_2Pb$ or Na_2PbO_2 solution that evolution of H_2S has ceased, filter, and reject the precipitate (silver and excess zinc). Test for I^- and Br^- in the filtrate with chlorine water or NaClO solution in the presence of benzene or chloroform, using 1-2 ml of the solution and proceeding as described on p. 453. The following tests can also be used for detecting I^- and Br^- ions:

(a) *iodide*, the test with KNO_2 in the presence of starch (Sec. 99, 5);

(b) *bromide*, the fuchsin test after oxidation of Br^- to Br_2 (Sec. 98, 4).

Note. Very small amounts of solution should be taken when testing for I^- and Br^- ions; otherwise too much chlorine water or NaClO solution is needed to displace all the iodine, and the Br^- ion can easily be missed.

Sometimes the conversion of CNS^- ions to HCN by the action of zinc and H_2SO_4 may be incomplete. The presence of thiocyanate ions would interfere with detection of I^- and Br^-, as the chlorine water would be consumed for oxidation of CNS^-. Therefore if the chlorine water test for I^- and Br^- is negative, put a drop of KI or KBr solution into the same test tube. If the layer of organic solvent acquires the appropriate colour after shaking, the solution does not contain any interfering substances and the inference that I^- and Br^- are absent must be correct.

On the other hand, if the I^- or Br^- ions introduced into the solution cannot be detected, the solution must contain a reducing agent (CNS^- ions or H_2S). In that case take another portion of the filtrate after separation of metallic silver according to 7 and oxidize the reducing agent in it by means of $KMnO_4$ in the presence of H_2SO_4. Add the permanganate, in the fume cupboard, *until a single drop* of $KMnO_4$ produces a purple or yellowish brown colour. Remove the colour by adding 1-2 drops of *dilute* $Na_2S_2O_3$ solution (*an excess is detrimental*) and then test the solution for I^- and Br^- in the usual way.

THIRD GROUP OF ANIONS

The anions of Group III include NO_3^- (nitrate), NO_2^- (nitrite), CH_3COO^- (acetate), MnO_4^- (permanganate), and others. *The distinguishing feature of this group is that the barium and silver salts of these anions are soluble, so that Group III anions are not precipitated by* $AgNO_3$ *or* $BaCl_2$. The least soluble of the silver salts are $AgNO_2$ and CH_3COOAg, and they may be precipitated from fairly concentrated solution. However, they dissolve readily on dilution with water and heating. There is no common group reagent for Group III. The anions NO_2^-, NO_3^- and CH_3COO^- are colourless, and MnO_4^- is purplish violet.

105. Reactions of Nitrate, NO_3^-

The NO_3^- ion is the anion of nitric acid, HNO_3, which is one of the strongest mineral acids. Nitric acid is also a fairly powerful oxidizing agent, capable of oxidizing many different reducing agents. It is therefore used in analysis for dissolving various metals and alloys which are insoluble in HCl and H_2SO_4, for dissolving many sulphides, etc. Its usual reduction products are either nitrogen dioxide, NO_2, or nitric oxide, NO. Oxidation of various substances by concentrated HNO_3 results in formation of the former, while the latter is obtained when the dilute acid is used. In some cases the reduction of nitric acid can go further, with formation of free nitrogen, N_2, or even of ammonia, NH_3 (which forms the salt NH_4NO_3 with excess acid).

All the salts of HNO_3 (nitrates) are soluble in water except the basic nitrates of bismuth and mercury and nitrates of certain organic bases. Therefore oxidation reactions are used almost exclusively for detection of the NO_3^- ion.

1. Reaction with Copper and Sulphuric Acid. Add concentrated H_2SO_4 and a piece of metallic copper to a solution of a nitrate. Heat the test tube. A brown gas (NO_2) is evolved; it is seen most easily if the test tube is held over a sheet of white paper and viewed from above. *First make sure that the reaction is not too violent.* The equations are:

$$2NO_3^- + 8H^+ + 3Cu = 3Cu^{++} + 4H_2O + 2NO\uparrow$$

$$2NO + O_2 \text{ (atmospheric)} = 2NO_2$$

2. Reaction with $FeSO_4$. Add a small amount of nitrate solution to $FeSO_4$ solution and mix. Now tilt the test tube and pour concentrated H_2SO_4 cautiously into it down one side, avoiding mixing of the liquids as far as possible. A brown ring appears at the bound-

ary between the H_2SO_4 and $FeSO_4$ layers:

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO\uparrow$$

The NO formed in the reaction gives an unstable complex compound, brown in colour, with the formula $[Fe(NO)]SO_4$ when it reacts with $FeSO_4$.

Iodides and bromides interfere, because in their presence free I_2 or Br_2 is evolved, similar in colour to the ring. The ions CrO_4^{--}, MnO_4^-, $[Fe(CN)_6]^{---}$, $[Fe(CN)_6]^{==}$, CNS^-, $S_2O_3^{--}$ and SO_3^{--} should also be absent.

The NO_2^- ion also gives this reaction, which takes place with dilute H_2SO_4 and even with CH_3COOH.

3. Reduction to Ammonia. Add concentrated alkali solution to a nitrate solution in a test tube. Put in a small amount (as much as can be held on the tip of a pen-knife) of zinc dust. Plug the test tube (not too tightly) with a piece of cotton wool about 1 cm thick to hold back splashes of alkali carried out by the escaping gas. Put a piece of moist litmus or phenolphthalein paper on top of the plug and heat the test tube.

Under these conditions the NO_3^- ion is reduced to NH_3, which turns litmus blue and phenolphthalein red. The equation is

$$NaNO_3 + 4Zn + 7NaOH = NH_3\uparrow + 4Na_2ZnO_2 + 2H_2O$$

If aluminium powder is used instead of zinc, the reaction is very violent and must therefore be performed *without heating and with dilute alkali solution.* The equation is

$$3NO_3^- + 8Al + 5OH^- + 2H_2O = 3NH_3\uparrow + 8AlO_2^-$$

The presence of NH_4^+ interferes with detection of NO_3^- by this reaction; the solution must first be boiled with alkali to remove ammonium ions. All other anions containing nitrogen, such as NO_2^-, CNS^-, $[Fe(CN)_6]^{==}$ and $[Fe(CN)_6]^{---}$, which are also reduced by aluminium to NH_3, also interfere.

4. Reaction with $MnCl_2$. When a solution of a nitrate is heated with twice its own volume of saturated $MnCl_2$ solution in concentrated HCl, it turns dark brown owing to formation of complex $[MnCl_6]^{--}$ ions:

$$3MnCl_2 + 12HCl + 2HNO_3 = 3H_2[MnCl_6] + 4H_2O + 2NO\uparrow$$

Certain other oxidizing agents, such as MnO_4^- and CrO_4^{--} ions, also give this reaction. The NO_2^- ion gives a yellow colour due to NO_2 gas dissolved in the liquid.

5. Reduction of NO_3^- to NO_2^-. Nitrates are reduced to nitrites by metallic zinc in the presence of CH_3COOH:

$$NO_3^- + Zn + 2CH_3COOH = NO_2^- + Zn^{++} + 2CH_3COO^- + H_2O$$

The formation of NO_2^- can be confirmed by its characteristic reactions (Sec. 106).

6. Reaction with Diphenylamine, $(C_6H_5)_2NH$. Put 4-5 drops of diphenylamine solution in concentrated H_2SO_4 on a thoroughly washed and dried watch glass. Introduce a very small amount of nitrate solution on the tip of a clean glass rod, and stir. An intense blue colour appears in the presence of NO_3^- as the result of oxidation of diphenylamine by the nitric acid formed.

This reaction is also given by NO_2^-, CrO_4^{--}, MnO_4^-, $[Fe(CN)_6]^{---}$, Fe^{+++}, and other oxidizing agents with sufficiently high oxidation potentials. Any I^- ions present are oxidized by sulphuric acid to I_2, which may sometimes mask the colour due to NO_3^- ions.

7. Microcrystalloscopic Test. Add one drop of a 10% solution of the organic base known as nitron ($C_{20}H_{16}N_4$) in 5% acetic acid to a drop of nitrate solution. Characteristic clusters of needle-shaped

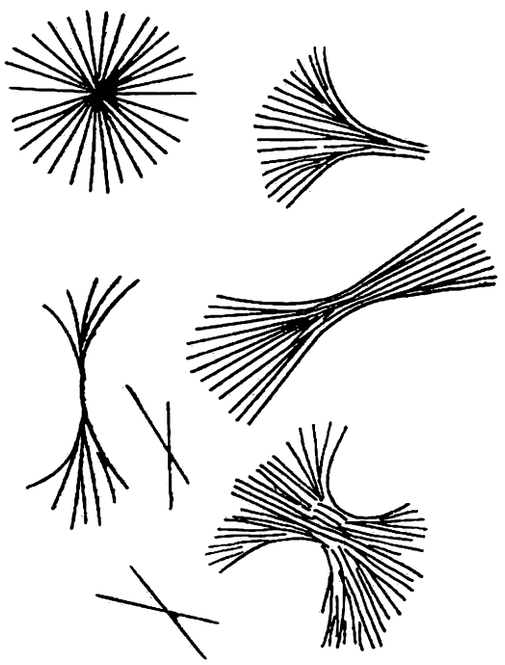


Fig. 46. Crystals of nitron nitrate

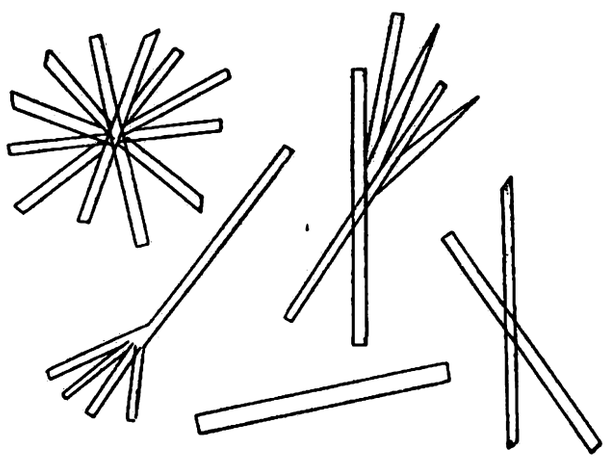


Fig. 47. Crystals of nitron nitrite

crystals of nitron nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$ are formed; their appearance under the microscope is shown in Fig. 46. The test will detect 0.025 μg of NO_3^-. The dilution limit is 1 : 120,000.

Of the anions studied here, NO_2^- (Fig. 47), CNS^- and I^- also form crystalline precipitates with nitron. However, these precipitates are easy to distinguish from the crystals formed by the NO_3^- ion.

106. Reactions of Nitrite, NO_2^-

The NO_2^- ion is the anion of nitrous acid, HNO_2. Free nitrous acid exists only in cold dilute aqueous solutions, as it decomposes very easily into the anhydride and water:

$$2HNO_2 = N_2O_3 + H_2O$$

Nitrous anhydride is also very unstable and exists only at low temperatures. At room temperature it decomposes immediately to form nitric oxide and nitrogen dioxide:

$$N_2O_3 = NO + NO_2$$

Nitrites are considerably more stable than HNO_2. They are all readily soluble in water. Silver nitrite, $AgNO_2$, is less soluble than the others but it dissolves easily on heating. Certain complex salts containing the NO_2^- ion, such as $K_3[Co(NO_2)_6]$, $(NH_4)_3[Co(NO_2)_6]$, etc., are sparingly soluble.

Unlike nitric acid, nitrous acid is a relatively weak acid ($K = 4 \times 10^{-4}$).

The nitrite ion gives all the tests of the nitrate ion described above (with the exception of 5). Nitrite can be distinguished from nitrate by the following tests.

1. **Acids** decompose all nitrites with formation of brown NO_2 gas:

$$2NaNO_2 + H_2SO_4 = Na_2SO_4 + 2HNO_2$$

$$2HNO_2 = NO_2\uparrow + NO\uparrow + H_2O$$

2. **Potassium iodide, KI,** in the presence of dilute H_2SO_4 is oxidized by nitrites to free I_2 (Sec. 99, 5). It will be remembered that other oxidizing agents with sufficiently high oxidation potentials, such as MnO_4^- CrO_4^{--}, $[Fe(CN)_6]^{---}$, AsO_4^{---} (in strongly acidic solution), and certain others, have the same effect on I^- ions.

3. **Action of $KMnO_4$.** Since nitrogen has an intermediate valency (+3) in HNO_2, the valency can be both increased and decreased. In other words, the NO_2^- ion can itself be oxidized and also act as an oxidizing agent (as in the reaction described above). It is oxidized by the action of potassium permanganate solution on a heated solution of a nitrite acidified by H_2SO_4:

$$5NO_2^- + 2MnO_4^- + 6H^+ = 5NO_3^- + 2Mn^{++} + 3H_2O$$

The colour of the $KMnO_4$ solution disappears as the result of this reaction. It will be remembered that $KMnO_4$ is also decolourized by many other reducing agents with sufficiently low oxidation potentials (such as S^{--}, SO_3^{--}, $S_2O_3^{--}$, $C_2O_4^{--}$, CNS^-, AsO_3^{---}.

$[Fe(CN)_6]^{=}$, I^-, Br^-). In alkaline solutions permanganate is not reduced by NO_2^- ions.

4. Colour Test. A very sensitive test for the NO_2^- ion is based on the formation of a brightly coloured azo dye. To carry out this test, add solutions of sulphanilic acid and α-naphthylamine* to a solution of a nitrite (neutral, or in acetic acid). A characteristic red colour appears in the presence of NO_2^-, either at once or after some time (dependent on the amount of NO_2^- present).

In the absence of NO_2^- this test can be used for detecting NO_3^- after reduction by zinc dust in the presence of CH_3COOH (Sec. 105, 5).

5. Removal of NO_2^- may be effected by careful heating of the solution with solid NH_4Cl or $(NH_4)_2SO_4$. The following reaction takes place:

$$NH_4^+ + NO_2^- = N_2\uparrow + 2H_2O$$

Urea, $CO(NH_2)_2$, in acid solution acts similarly to ammonium salts:

$$2NO_2^- + 2H^+ + CO(NH_2)_2 = 3H_2O + CO_2\uparrow + 2N_2\uparrow$$

Carry out this reaction as follows. Dissolve about 0.5 g of urea in 1 ml of nitrite solution, and add the resultant solution *by small portions* to 1 ml of 2 *N* H_2SO_4. *Do not add a fresh portion until the violent reaction caused by the preceding portion has stopped.* When all the solution has been added, leave the liquid to stand and then test a separate portion for NO_2^- with KI in the presence of starch.

It must be pointed out that during the removal of NO_2^-, especially by the action of ammonium salts, a small amount is usually oxidized to NO_3^-.

Nitrate can be detected in the presence of nitrite only after removal of NO_2^- ions from solution as described above.

It must be remembered, however, that because nitrites are easily oxidized solutions containing considerable amounts of nitrite almost invariably contain NO_3^- ions, so that a reliable test for this ion is hardly feasible.

Only *large amounts* of NO_3^- in the presence of small amounts of NO_2^- can be detected with certainty. A relatively insensitive test for NO_3^- (for example, the test with Cu and H_2SO_4 described in Sec. 105, 1) is used for this purpose, after preliminary removal of NO_2^- by the action of $CO(NH_2)_2$ or an ammonium salt. However,

---

* The formula of sulphanilic acid is $H_2N—C_6H_4—SO_3H$, and that of α-naphthylamine is $C_{10}H_7—NH_2$. The reaction product has the formula

$$H_2N—C_{10}H_6—N=N—C_6H_4—SO_3H$$

the presence of NO_3^- can be inferred with certainty only if the test is very distinct.

6. Microcrystalloscopic Test. Put a small grain of the substance to be tested for NO_2^- into a drop of solution containing the acetates of potassium, lead, and bivalent copper and acidified with CH_3COOH. Black cubic crystals of $K_2Pb[Cu(NO_2)_6]$, which we have already met (see Fig. 6, p. 90), are formed. The detectable minimum is 0.75 μg NO_2^-. The dilution limit is 1 : 1,500. The nitrate ion does not interfere.

107. Reactions of Acetate, CH_3COO^-

The acetate ion is the anion of acetic acid, CH_3COOH, which is a weak monobasic acid ($K = 1.86 \times 10^{-5}$). Most of its salts, the acetates, are readily soluble in water. Silver acetate is less soluble than the others, and certain basic salts such as $CH_3COO(OH)_2Fe$ and $CH_3COO(OH)_2Al$ are sparingly soluble.

1. Sulphuric acid displaces free CH_3COOH from acetates; the acetic acid volatilizes on heating and can be recognized by its characteristic smell. The test based on formation of free acetic acid can also be carried out by grinding the solid substance with a small amount of solid $NaHSO_4$ or $KHSO_4$.

2. Formation of Ethyl Acetate and Amyl Acetate. Add concentrated H_2SO_4 and ethyl alcohol to a solution of an acetate, or preferably to the solid salt, heat the mixture for 1-2 minutes on a water bath, and pour out the liquid into cold water in a beaker. The ethyl acetate formed, $CH_3COOC_2H_5$, is easily recognized by its pleasant smell.

The reaction is represented by the following equations:

$$2CH_3COONa + H_2SO_4 = Na_2SO_4 + 2CH_3COOH$$
$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$$

If amyl alcohol ($C_5H_{11}OH$) is used instead of ethyl alcohol, amyl acetate $CH_3COOC_5H_{11}$ is formed, with a pleasant smell of pear drops.

3. Ferric Chloride. Add a small amount of $FeCl_3$ to a solution of CH_3COONa; a red-brown colour due to formation of $(CH_3COO)_3Fe$ appears. If the solution is diluted with water and heated, the basic salt is precipitated:

$$(CH_3COO)_3Fe + 2H_2O = \downarrow CH_3COO(OH)_2Fe + 2CH_3COOH$$

The solution must be neutral and must not contain anions which precipitate ferric ion: CO_3^{--}, SO_3^{--}, PO_4^{---}, $[Fe(CN)_6]^{=}$, etc. (the CNS^- and I^- ions should also be absent; iodide is oxidized by Fe^{+++}

ions to I_2 which produces a red-brown colour similar to that expected in the reaction). All these ions can be removed by addition of $AgNO_3$ or Ag_2SO_4 solution to the neutral solution. However, this involves the use of considerable amounts of silver salts, and therefore the test should not be used unless absolutely necessary.

4. Reaction with Lanthanum Nitrate, $La(NO_3)_3$. Put one drop each of the acetate solution, 5% $La(NO_3)_3$ solution, and 0.01 *N* iodine on a watch glass. After 1 minute add one drop of 1 *N* NH_4OH and leave for a few minutes. In the presence of CH_3COO^- the drop of ammonia* becomes surrounded by a blue or bluish-brown ring, probably resulting from adsorption of iodine by basic lanthanum acetate. The SO_4^{--} and PO_4^{---} ions, which form sparingly soluble salts with lanthanum, interfere. Therefore SO_4^{--} and PO_4^{---} must first be precipitated by addition of $Ba(NO_3)_2$ or $BaCl_2$.

108. Reactions of Permanganate, MnO_4^-

The permanganate ion is the anion of permanganic acid, $HMnO_4$, containing septivalent manganese. Free permanganic acid exists only in aqueous solution. All its salts are easily soluble in water and the solutions have a purple-violet colour. Accordingly, all the tests for MnO_4^- are based on oxidation of various substances or ions. If the oxidation is performed in acid solution, the MnO_4^- ion is usually reduced to the cation Mn^{++}:

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$$

and the purple-violet colour of the MnO_4^- ion disappears.

In oxidation reactions in alkaline or neutral solutions the MnO_4^- ion is reduced only as far as Mn^{+IV}, precipitated as brown $MnO(OH)_2$:

$$MnO_4^- + 3H_2O + 3e = MnO(OH)_2 + 4OH^-$$

1. Oxidation Reactions of the MnO_4^- Ion. The oxidation potential of the MnO_4^-/Mn^{++} couple is very high, +1.51 V. Accordingly, in acid solution the MnO_4^- is one of the most powerful oxidizing agents. It oxidizes a large number of reducing agents, such as H_2S, sulphites, thiosulphates, iodides, bromides, chlorides**, arsenites, thiocyanates, ferrocyanides, oxalates, nitrites, hydrogen peroxide***, certain cations (Fe^{++}, Sn^{++}, Sb^{+++}, etc.), many organic

---

* The liquid should not be stirred after addition of NH_4OH.

** Iodide ions are oxidized very easily even in the cold; Br^- ions are oxidized with more difficulty in the cold but easily on heating; Cl^- ions are not oxidized to any appreciable extent by MnO_4^- in the cold. On heating in the presence of mineral acids Cl^- is oxidized, although with some difficulty. In the presence of acetic acid oxidation is very slight, even on heating.

*** Hydrogen peroxide acts as a reducing agent in this reaction (see p. 250, 5).

substances such as benzidine and diphenylamine, etc. The equations for these reactions were given in the descriptions of the reactions of the respective ions.

The standard oxidation potential of the couple MnO_4^-/MnO_2 in alkaline solution is considerably lower than that of MnO_4^-/Mn^{++}. It is only +0.54 V; therefore MnO_4^- ions are far less active as oxidizing agents in alkaline than in acid solutions. For example, a number of reducing agents can be readily oxidized by MnO_4^- ions in acid but not in alkaline solution. They include NO_2^-, Cl^-, and Br^-. The anions I^-, S^{--}, SO_3^{--}, $S_2O_3^{--}$, AsO_3^{---}, CNS^-, $[Fe(CN)_6]^{=}$, which are stronger reducing agents, are oxidized by MnO_4^- in alkaline as well as in acid solution. As already stated we will use the action of $KMnO_4$ in alkaline solution in preliminary tests for the presence of the above-named reducing anions.

2. Action of Acids. Dilute acids do not react with permanganates to any appreciable extent. Concentrated H_2SO_4 reacts with dry permanganates to give permanganic anhydride, Mn_2O_7, which is a brownish-green oily liquid. Mn_2O_7 decomposes readily (explosively) on gentle heating to give MnO_2 and oxygen. The heat liberated by the action of H_2SO_4 is usually sufficient to cause this explosion. The equations are:

$$4KMnO_4 + 2H_2SO_4 = 2K_2SO_4 + 2Mn_2O_7 + 2H_2O$$

$$2Mn_2O_7 = 4MnO_2 + 3O_2 \uparrow$$

3. Dry-Way Test. Dry permanganates are decomposed by heat; oxygen is evolved and can be detected by relighting a glowing splint introduced into the test tube (or crucible):

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2 \uparrow$$

The compound formed, K_2MnO_4 (potassium manganate), is a derivative of sexivalent manganese.

The equation for the reaction can be derived as follows by the electron-ion method:

$$MnO_4^- - e = MnO_2 + O_2$$

$$MnO_4^- + e = MnO_4^{--}$$

$$2MnO_4^- = MnO_4^{--} + MnO_2 + O_2 \uparrow$$

The molecular equation given in the text follows from this equation.

109. Analysis of Mixtures of Anion Groups I, II and III

Systematic group analysis of anions in the sense defined earlier (p. 428) is rarely necessary in analytical practice. In most cases anions are detected by the fractional method, i.e., in separate

portions of the unknown solution and not in any special sequence. Separation reactions are required only in relatively rare instances. The most important of these were discussed in Sec. 92 (detection of PO_4^{---}, AsO_4^{---} and AsO_3^{---}), in Sec. 99 (detection of Cl^-, Br^- and I^-), in Sec. 100 (detection of S^{--}, SO_3^{--}, $S_2O_3^{--}$ and SO_4^{--}), and in Sec. 104 (detection of all anions of Group II).

Although no particular sequence of the tests is obligatory in anion analysis, and the sequence may be varied, it is nevertheless advisable for the sake of convenience and speed to keep to a definite plan. It is preferable to start the analysis with a number of preliminary tests in order to establish the absence of certain anions and so simplify the subsequent analysis.

These tests, described in detail below, include (a) tests by the group reagents $BaCl_2$ and $AgNO_3$; (b) tests for reducing agents (by means of $KMnO_4$ and I_2 solutions) and for oxidizing agents (with KI solution); (c) tests for evolution of gases on addition of 2 *N* H_2SO_4. When convenient, these preliminary tests should be accompanied by tests for certain individual anions (SO_4^{--}, SO_3^{--}, $S_2O_3^{--}$ and Group II anions).

After the preliminary tests, and after it has been shown that certain anions cannot be present in the unknown solution, the next stage is to test for the anions (out of those not already detected) which may be present.

As in different cases different tests have to be used for the same anions, the experimental techniques are not described in the analytical procedure given below, and only the applicability of various tests is considered. Therefore the descriptions given in the text should be used in practical analysis.

It must be remembered that the solution used for testing for anions must not contain any cations other than K^+, Na^+ and NH_4^+. All other cations, starting with Mg^{++}, form insoluble salts with many anions, interfere with their detection, and must previously be removed by boiling with sodium carbonate. This operation is discussed in more detail in Sec. 114.

To avoid excessive complication, we do not consider here those relatively rare cases, usually of no practical significance, when the solution contains oxidizing and reducing agents which are mutually incompatible in acid solutions. The student can use the information in this book for understanding the simplest of such cases for himself.

The specialized literature must be consulted in more complicated cases.

ANALYSIS OF MIXTURES OF ANIONS OF GROUPS III-I

A. PRELIMINARY TESTS

1. Reaction of the Unknown Solution. If the solution has an acid reaction ($pH \leqslant 2$), it cannot contain anions of volatile or unstable acids, such as CO_3^{--} and $S_2O_3^{--}$. If the acid solution is also odourless, the anions S^{--}, SO_3^{--} and NO_2^- are likewise absent.

Note. If an aqueous solution obtained from a solid mixture is acid, it cannot be concluded that the CO_3^{--} ion is absent, because when the solid mixture is dissolved, reactions accompanied by complete decomposition of carbonates and evolution of CO_2 may occur. For example, the following reaction takes place when a mixture of Na_2CO_3 and $Al_2(SO_4)_3$ is dissolved:

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = \downarrow 2Al(OH)_3 + 3Na_2SO_4 + 3CO_2 \uparrow$$

If aluminium sulphate is present in excess in the mixture, then it confers an acid reaction to the solution. It follows that in the case of solid mixtures the test for the CO_3^{--} ion must be carried out with a separate portion of the solid.

2. Test for Group I Anions. Add $BaCl_2$ solution to a separate portion of the neutral or slightly alkaline solution ($pH \approx 7$-9)*. Formation of a precipitate indicates the presence of Group I anions**.

3. Tests for Group II Anions. Add $AgNO_3$ solution to a separate portion of the unknown solution. If a precipitate forms, acidify with HNO_3 solution. If the precipitate does not dissolve, Group II anions may be present (or $S_2O_3^{--}$, which precipitates Ag_2S with the Ag^+ ion, and sulphur with HNO_3). In that case test a separate portion of the solution for Group II anions as described in Sec. 104 (or on p. 455, if CNS^-, $[Fe(CN)_6]^{=}$ and $[Fe(CN)_6]^{---}$ are known to be absent).

4. Tests for Reducing Anions. (a) To 1 ml of the solution add 2 *N* caustic soda and dilute $KMnO_4$ solution (see Sec. 89, 5). In the absence of a precipitate heat the solution on a water bath for 1 minute. A brown precipitate of $MnO(OH)_2$ indicates the presence of reducing anions (S^{--}, SO_3^{--}, $S_2O_3^{--}$, I^-, AsO_3^{---}, CNS^-, $[Fe(CN)_6]^{=}$ and possibly*** $C_2O_4^{--}$).

(b) If the previous test showed the presence of reducing agents. acidify another portion of the solution with H_2SO_4 and add drop

---

* Acid solutions must first be neutralized with $Ba(OH_2)$.

** The anions $S_2O_3^{--}$ and BO_2^{--} may be present even if a precipitate is not formed, as they are precipitated by Ba^{++} only from fairly concentrated solutions.

*** The $C_2O_4^{--}$ ion reduces $KMnO_4$ in alkaline solution slowly and therefore its absence cannot be concluded if no precipitate of $MnO(OH)_2$ forms. Sometimes the solution turns brown without a precipitate being formed. This may be due either to formation of colloidal $MnO(OH)_2$ or to precipitation of free I_2.

by drop a dilute solution of iodine coloured blue by starch. If the colour disappears, S^{--}, $S_2O_3^{--}$ or SO_3^{--} anions are present.

5. Test for Oxidizing Anions. Acidify 1 ml of the solution with 2 *N* H_2SO_4 and add 1 ml of benzene or chloroform and 10-20 drops of KI. If the solvent layer turns violet on shaking, oxidizing anions are present (MnO_4^-, CrO_4^{--}, NO_2^-, $[Fe(CN)_6]^{---}$ or possibly* AsO_4^{---}).

If the test gives a negative result, add a saturated solution of $MnCl_2$ in concentrated HCl to another portion of the solution and heat for 1 minute. A black or brown colour (see p. 470) indicates the presence of NO_3^- ions**. Confirm this by other tests for nitrate (action of diphenylamine, etc.).

6. Test for Gas Evolution. Treat a portion of the solution (or, preferably, a small portion of the solid substance) with 2 *N* H_2SO_4 and shake the test tube slightly by tapping its lower end gently with the finger. If no gas bubbles appear, warm the test tube. Evolution of gases (CO_2, SO_2, H_2S, NO_2) indicates the possible presence of the ions CO_3^{--}, S^{--}, SO_3^{--}, $S_2O_3^{--}$, NO_2^-.

Note. The gases should be identified if possible. Their properties are:
(a) CO_2—a colourless and odourless gas which turns lime water cloudy***;
(b) SO_2—a gas with the smell of burning sulphur; it decolourizes**** dilute I_2 and $KMnO_4$ solutions;
(c) H_2S—a gas with the smell of bad eggs, which blackens paper moistened with $(CH_3COO)_2Pb$ or Na_2PbO_2 solution;
(d) NO_2—a red-brown gas with a characteristic sharp smell.

B. TESTS FOR INDIVIDUAL ANIONS

Test as described below for any anions (unless already detected) the possible presence of which is indicated by the preliminary tests.

7. Tests for S^{--}, $S_2O_3^{--}$, SO_3^{--} and SO_4^{--} Ions. If the test for reducing agents with iodine solution (4, *b*) gave a positive result, test for S^{--}, $S_2O_3^{--}$, SO_3^{--} and SO_4^{--} in a separate portion of the solution as described on p. 458. If the I_2 test is negative, test for SO_4^{--} by addition of $BaCl_2$ to a separate portion of the solution. A white precipitate of $BaSO_4$, insoluble in *dilute****** HCl, proves the presence of SO_4^{--}.

---

* The AsO_4^{---} ion oxidizes I^- only at a sufficiently high H^+ ion concentration. Therefore it cannot be assumed from a negative result in this test that AsO_4^{---} is absent.

** A yellow colour appears in the presence of NO_2^-, due to NO_2 gas dissolved in the liquid.

*** SO_2 may also have this effect.

**** H_2S also decolourizes I_2 and $KMnO_4$.

***** Concentrated HCl must not be used, as it may cause precipitation of $BaCl_2$ (action of the common Cl^- ions; see Sec. 25).

8. Test for CO_3^{--} Ions. Put a small amount of the solid (or 1-2 ml of solution) to be tested in the apparatus shown in Fig. 43 (p. 436). If previous tests showed the presence of SO_3^{--} or $S_2O_3^{--}$, add H_2O_2 (3%) to oxidize these ions. Then add 2 *N* HCl and proceed as outlined on p. 436.

9. Tests for PO_4^{---}, AsO_4^{---} and AsO_3^{---} Ions. (a) If AsO_4^{---} or AsO_3^{---} cannot be present, test for PO_4^{---} with ammonium molybdate solution. Warm 1 ml of the solution for a few minutes with 2 ml of 6 *N* HNO_3 to oxidize reducing agents, add ammonium molybdate solution in excess, and warm to 40-50°. If no precipitate appears, add a few crystals of NH_4NO_3 and leave to stand. Formation of a yellow precipitate of $(NH_4)_3H_4[P(Mo_2O_7)_6]$ indicates the presence of PO_4^{---}.

(b) If the presence of AsO_4^{---} or AsO_3^{---} is possible, proceed as described on p. 439.

10. Tests for $C_2O_4^{--}$, F^-, BO_2^- Ions. (a) Acidify a separate portion of the solution with CH_3COOH (to pH $\approx$ 4-5), add excess $CaCl_2$ solution, and heat. Formation of a precipitate (CaC_2O_4 or CaF_2) indicates the possible presence of $C_2O_4^{--}$ or F^- ions. Filter off the precipitate, *wash it thoroughly* (to remove adsorbed reducing agents) and treat with 2 *N* H_2SO_4 on heating. If the precipitate does not dissolve completely, separate off the residue, heat the filtrate to 60-70°, and add dilute (0.01 *N*) $KMnO_4$ drop by drop*. If the colour fades, $C_2O_4^{--}$ is present.

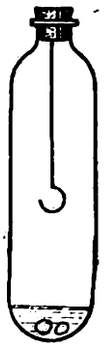


Fig. 48. Apparatus for detection of gases formed in reactions

(b) If the previous test indicated the possible presence of F^-, confirm its presence as follows. Put a small amount of the solid substance** into the *dry* flask of the apparatus shown in Fig. 48 and add a few drops of concentrated H_2SO_4. Then introduce a drop of water in a platinum wire loop into the vessel and leave to stand. Gaseous SiF_4 is formed in the presence of fluoride; it reacts with water and turns the drop cloudy owing to formation of silicic acid.

In the absence of phosphates and oxalates, F^- can be detected in solution by the spot test with alizarin and zirconyl nitrate (Sec. 94, 5).

(c) To test for BO_2^-, put 1 ml of the solution into a porcelain crucible and treat it with concentrated H_2SO_4. Add a small amount of ethyl (or methyl) alcohol and set it alight. A green-edged flame indicates the presence of BO_2^-. Borate can also be detected by the

* It is helpful to add a drop of $MnSO_4$ solution in order to accelerate the reaction.

** If a solution is being analyzed, a small portion must be evaporated to dryness in a crucible or porcelain basin.

test with CaF_2 and sulphuric acid (Sec. 93, 4, *b*) or with turmeric paper (Sec. 93, 3).

11. Test for SiO_3^{--} Ions. Add 2 *N* ammonia to 0.5-1 ml of the solution until the liquid smells of ammonia, followed by saturated NH_4Cl solution, and heat for a few minutes on the water bath. A white gelatinous precipitate of silicic acid indicates the presence of SiO_3^{--}. The test is conclusive only in the absence of cations of amphoteric elements (Al, Sn, Sb). In the presence of such elements a confirmatory test must be carried out with methylene blue (see Sec. 95, 4), or SiO_3^{--} must be confirmed by the microcrystalloscopic test with formation of $Na_2[SiF_6]$ crystals (Sec. 95, 5).

12. The test for CrO_4^{--} is carried out only if the solution is of a yellow or orange colour.

Add a drop of phenolphthalein to 0.5-1 ml of the solution; if the liquid turns red, add 2 *N* H_2SO_4 drop by drop until colourless. Add one more drop of acid followed by some amyl alcohol and a few drops of hydrogen peroxide, and mix immediately. A blue ring due to formation of perchromic acid (H_2CrO_6) proves the presence of CrO_4^{--}.

13. Test for MnO_4^- Ions. A purple-violet colour (or pink at low concentrations of MnO_4^-) indicates the presence of MnO_4^-. To confirm, add the solution drop by drop to $(NH_4)_2C_2O_4$ solution acidified with H_2SO_4 and heated to 70°. If the colour fades, MnO_4^- is present.

The chromate ion interferes in the test for MnO_4^-, and must be removed by precipitation in the form of $BaCrO_4$ through addition of $Ba(OH)_2$ solution.

14. Tests for I^- and Br^- ions are carried out in different ways, dependent on the presence or absence of reducing anions (S^{--}, SO_3^{--}, $S_2O_3^{--}$).

a. Reducing ions absent. Acidify about 1 ml (not more) of the solution with 2 *N* H_2SO_4 and test for I^- and Br^- by addition of chlorine water or NaClO in the presence of benzene (Sec. 99, 4). If a large amount of I^- is present, it should be removed by boiling with KNO_2 in acid solution (Sec. 99, 5) before testing for Br^-.

b. Reducing ions present. In the presence of S^{--}, SO_3^{--} or $S_2O_3^{--}$ ions, chlorine water is first consumed for oxidation of these ions. However, as the concentration of free Cl_2 in chlorine water is low, a large volume may be required for this oxidation and it is easy to "miss" I^- and Br^- ions. Therefore S^{--}, SO_3^{--} and $S_2O_3^{--}$ must first be oxidized by $KMnO_4$ in acid solution*. Acidify

---

* Permanganate is a convenient oxidizing agent because it can be obtained in much more concentrated solutions than Cl_2. Moreover, the colour change indicates the course of oxidation.

a small portion (about 1 ml) strongly with dilute H_2SO_4 and add $KMnO_4$ solution drop by drop with continuous stirring until a purple (excess $KMnO_4$) or yellowish-brown (liberation of I_2 or Br_2) colour appears and persists after shaking. To remove the colour add very dilute $Na_2S_2O_3$ (the reagent solution dilute 10-20 times) drop by drop, stirring continuously; avoid the slightest excess of $Na_2S_2O_3$, as it interferes with the tests for I^- and Br^-. The solution is now free from reducing agents; test it for I^- and Br^- as described above (a).

The above method for removing reducing anions is rapid and gives very good results, but only with very careful and precise working.

If I^- and Br^- are not detected, the following procedure may be recommended to confirm that the operations have been carried out correctly. Put one or two drops of KI solution into the test tube in which the test for I^- and Br^- was performed, and which therefore already contains benzene and chlorine water. If the violet colour characteristic of iodine appears on shaking, the solution does not contain anything which can interfere with detection of I^- and Br^-, and their absence is confirmed. On the other hand, if the test for iodide is negative after addition of I^- ions, it follows that either reducing agents have not been completely removed or an excess of $Na_2S_2O_3$ had been used. In that case the oxidation procedure must be repeated with a fresh portion of the unknown solution.

15. Test for NO_2^- Ions. Evolution of brown NO_2 gas on addition of H_2SO_4 to the solution indicates the presence of NO_2^-. To confirm, put a drop of the solution, neutral or acidified with acetic acid (pH = 4-7), on a spot plate and add one drop each of sulphanilic acid and α-naphthylamine solutions (see Sec. 106, 4). A red colour (appearing immediately or after some time) confirms the presence of NO_2^-.

16. Tests for NO_3^- Ions. *a. In the absence of nitrite.* Convert NO_3^- into nitrite (by heating with metallic zinc and acetic acid; see Sec. 105, 5) and test for NO_2^- by the colour reaction with sulphanilic acid and α-naphthylamine (see above). A positive test for nitrite in this case indicates the presence of NO_3^- in the original solution.

In the absence of CNS^-, $[Fe(CN)_6]^{=}$ and $[Fe(CN)_6]^{---}$, nitrate can also be detected by reduction to ammonia (see Sec. 105, 3). First, test for NH_4^+; if present, remove ammonium ions by evaporation of a few millilitres of the solution with excess NaOH almost to dryness in a crucible (*cautiously*, to avoid splashing). Cool, dilute with water, transfer the liquid to a test tube, add 2 *N* NaOH and a small amount of aluminium powder, and warm slightly. Put a plug of cotton wool in the mouth of the test tube (to catch any splashes) with a piece of moist phenolphthalein paper on top. Leave to stand. If the reaction is too violent, cool the test tube in water. Reddening of the paper (formation of NH_3) indicates the presence of NO_3^- ions in the original solution.

In the absence of other oxidizing anions (MnO_4^-, CrO_4^{--}, $[Fe(CN)_6]^{---}$ and NO_2^-) the most convenient test for NO_3^- is with diphenylamine. Put 4-5 drops of a solution of diphenylamine in concentrated H_2SO_4 on a clean and dry watch glass, introduce a very small amount of the unknown solution on the tip of a clean glass rod, and stir. An intense blue colour indicates the presence of NO_3^-. A large amount of I^- ions may interfere.

Finally, the microcrystalloscopic test for NO_3^- with nitron (see Sec. 105, 7) is very convenient.

b. In the presence of nitrite. In such cases considerable amounts of NO_3^- can be detected after removal of nitrite as described in Sec. 106, 5.

17. Tests for CH_3COO^- Ions. (a) To 1 ml of the solution add 1 ml of ethyl alcohol, C_2H_5OH, and 1 ml of concentrated H_2SO_4. The characteristic smell of ethyl acetate indicates the presence of CH_3COO^-.

(b) Grind a small amount of the solid substance thoroughly in a small mortar with solid $NaHSO_4$ or $KHSO_4$. A smell of acetic acid proves the presence of CH_3COO^-.

(c) If lanthanum nitrate is available, the test described in Sec. 107, 4 in the presence of I_2 and NH_4OH may be used. Sulphate and phosphate ions must first be precipitated by Ba^{++} ions.

QUESTIONS AND PROBLEMS

1. How are anions subdivided into groups? What are the characteristics of each group?
2. Name the group reagents for anion Groups I and II.
3. How does the analysis of anions differ from analysis of cations? What part is played by the group reagents?
4. If $BaCl_2$ does not give a precipitate with a solution, can it be concluded that Group I anions are absent without a preliminary test for the acidity of the solution?
5. Can concentrated rather than dilute hydrochloric acid be used in testing for SO_4^{--}? Explain.
6. Describe the action of acids on sulphites. What tests can be used to detect SO_2?
7. What is the action of metallic zinc on sulphites? Write the equation.
8. Describe how (a) $S_2O_3^{--}$ can be detected in the presence of SO_3^{--}; (b) the two ions can be separated.
9. Describe the tests for sulphur-containing anions if they may be present simultaneously.
10. Explain why the turbidity formed when CO_2 is passed through lime water finally disappears.
11. What ions interfere in tests for CO_3^{--}? Describe the procedure if these ions are present.
12. Describe the tests for distinguishing between AsO_3^{---} and AsO_4^{---} ions.
13. Describe the separation of AsO_4^{---} from PO_4^{---} ions. How can both these ions be detected without separation?

14. State the most important reactions of the SiO_3^{--} ion, and write the equations.

15. If a precipitate is formed when $AgNO_3$ is added to a neutral unknown solution, is this conclusive evidence of the presence of Group II anions?

16. Describe how Cl^- may be detected in the presence of Br^- and I^-.

17. Describe the tests for I^- and Br^- ions.

18. Which of the anions Cl^-, Br^- and I^- is most easily oxidized, and why? Give facts in confirmation of your answer.

19. Describe tests for S^{--} ions in sulphides which are (a) decomposed by acids; (b) not decomposed by acids.

20. Explain why, in testing for Cl^- in the presence of Br^- and I^- by the action of ammonium carbonate or ammoniacal silver nitrate on precipitated silver salts, it is necessary to ensure complete precipitation of these ions by Ag^+ ions.

21. Addition of $AgNO_3$ to an unknown solution gives (a) a black precipitate; (b) a precipitate which gradually turns black. What anions are indicated?

22. Which anions interfere with detection of I^- and Br^- ions by the action of chlorine water, and why? Describe the procedure to be used if these anions are present.

23. Name the most important tests for the NO_3^- ion, and write the equations.

24. Which tests for NO_3^- ions cannot be used in the presence of I^- or Br^- ions? Give reasons.

25. How may NO_2^- ions be distinguished from NO_3^-?

26. Is it possible to detect NO_3^- ions in the presence of NO_2^- by any of the tests described in this book?

27. Describe how NO_2^- ions may be removed from solution. Write the equations.

28. How can the CH_3COO^- ion be detected? What anions interfere in the different tests, and how should the tests be carried out in their presence?

CHAPTER IX

General Course of Analysis (Detection of Cations and Anions)

110. Preliminary Observations and Preparation of the Substance for Analysis

Complete analysis of any substance must be preceded by a thorough physical investigation.

If the substance is a solution, note its colour and odour and test its reaction to litmus. If a precipitate is present, note its colour and appearance.

Solid non-metallic samples must be carefully examined through a magnifying glass. Quite often it is possible in this way not only to establish that the sample is heterogeneous but also to obtain an idea of the probable number of constituents in it. The colour, shape, and size of the particles present in the sample should be noted. The colour of the particles, which may indicate the presence of certain elements, is an especially important sign. For example, the presence of blue crystals in the sample suggests the presence of copper salts; pink crystals may indicate cobalt or manganese salts, etc.

Of course, no final conclusions can be drawn from such observations. Nevertheless, they are useful because in conjunction with the analytical results they increase confidence in the analysis.

After the physical investigation, the sample must be prepared for analysis. Solids are thoroughly powdered to make the subsequent treatment with solvents easier. Powdering is necessary also because uniform mixing of the individual constituents is ensured only if a heterogeneous sample is thoroughly subdivided.

Substances which break up easily are ground in a porcelain or an agate mortar until a fine powder is obtained. Harder substances, such as various minerals, are first broken up into the smallest possible pieces in a steel mortar, and then ground in an agate mortar. In such cases the required fineness is often not achieved at once. Therefore the fine particles are separated from time to time by means of a fine screen, and the residue on the screen is ground again in the mortar. This procedure is continued until the whole sample to be analyzed passes through the screen. It is essential to achieve this, because the harder particles may differ in chemical composition from those passing through the screen. Therefore if the powdering is not taken to the end there is a risk of obtaining erroneous

analytical results. Metals or alloys must be converted into filings or shavings by means of suitable tools.

The substance prepared for analysis (if it is not a metal or alloy) is divided into three portions. One is used for detection of cations, the second for detection of anions, and the third is for preliminary tests and as a reserve if the necessity of checking the analytical results arises.

111. Preliminary Tests

Before systematic analysis, a series of preliminary tests should be carried out on separate portions of the sample. These tests give certain indications which may be useful for selecting the best method of dissolving the substance or may make the analysis easier*.

The following preliminary tests for cations are considered here: (a) heating of the substance with sodium carbonate on charcoal; (b) bead tests; (c) flame colour test. Preliminary tests for anions were described earlier (Sec. 109, 1-6) and are not repeated here.

1. Heating with Sodium Carbonate on Charcoal. Make a small cavity with the aid of a knife in a charcoal block, put into it a small amount of a mixture of the unknown substance with double the amount of anhydrous Na_2CO_3, and heat it in the *reducing flame* of a blow-pipe (Fig. 49). It will be remembered that a reducing flame is obtained if the tip of the blow-pipe is placed at the *outer edge* of a luminous burner flame, and the flame is blown gently in a sloping downward direction towards the cavity in the charcoal. The flame is merely deflected and remains luminous. Because of the presence of incandescent carbon particles in it, this flame reduces substances which come into contact with it. On the other hand, if we put the blow-pipe inside the burner flame and blow more strongly, we obtain a non-luminous oxidizing flame.

The following effects usually occur when the substance is heated with sodium carbonate by a reducing flame on charcoal. First, the salt is converted into a carbonate as the result of double decomposition; for example

$$PbCl_2 + Na_2CO_3 = PbCO_3 \downarrow + 2NaCl$$

Most carbonates, however, decompose when heated to high temperatures to form the corresponding oxides and carbon dioxide. In this instance

$$PbCO_3 = PbO + CO_2$$

* If the sample for analysis is a solution, a part is evaporated to dryness on a water bath and separate portions of the dry residue are used for preliminary tests.

The oxide formed is in most cases reduced immediately by the incandescent carbon particles to the free metal, e.g.,

$$PbO + C = Pb + CO$$

As a result, a bright "button" or bead of the fused metal appears in the cavity, or an infusible spongy mass if the metal is refractory. If the metal is volatile, some of it may be converted into vapour which is oxidized again by atmospheric oxygen on leaving the flame.

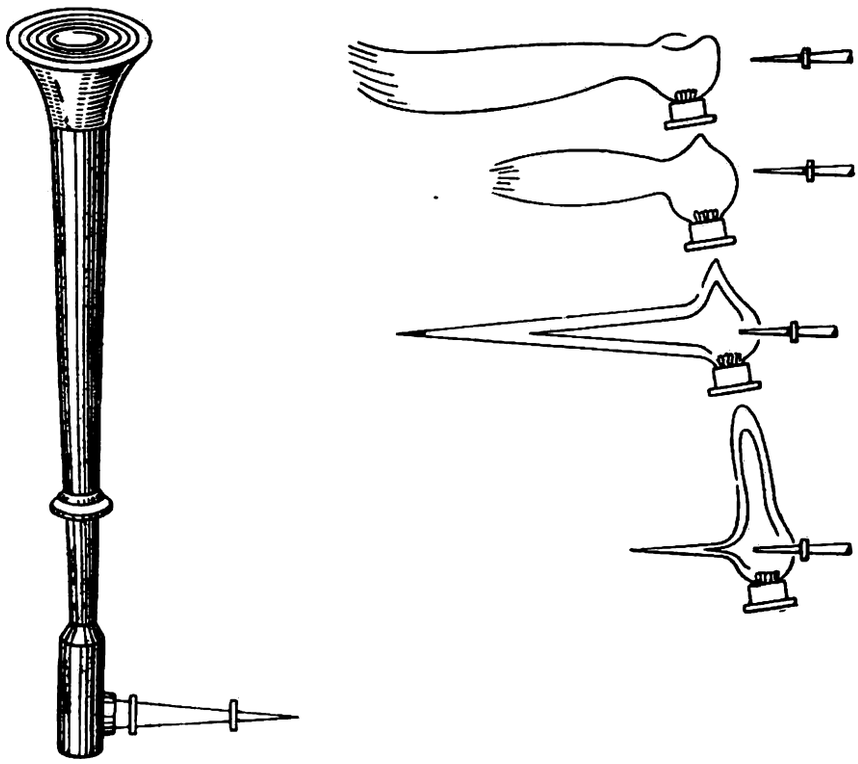


Fig. 49. Blow-pipe and its use

Consequently various coloured oxide deposits may appear on the cold regions of the charcoal near the cavity. For example, a yellow deposit of PbO is formed in the presence of lead, a white deposit (yellow when hot) of ZnO in the presence of zinc, etc. The most volatile metals, such as zinc, cadmium, and arsenic, do not form beads at all, because they volatilize completely and form deposits of the corresponding oxides.

In carrying out these tests it should be remembered that good results are obtained only if the blowing is even and continuous. To achieve this, practise blowing while breathing through the nose.

Sometimes the metal particles formed during the test are so fine that they are difficult to see. In such cases the contents of the cavity should be cut out with a knife and ground cautiously in a mortar with light pressure and careful impacts. If water is then poured over the powdered substance, the heavier metal grains remain on the

bottom of the mortar while the light carbon particles are washed away by the flowing water.

The metal beads obtained in this test are classified as malleable and brittle. A malleable bead is flattened out under pressure from a solid object such as a pestle or hammer, whereas a brittle one can be ground to a powder (in an agate mortar).

Table 30 gives the possible test results and their significance.

Table 30

Heating with Sodium Carbonate on Charcoal

Effects in charcoal cavity	Effects on cold charcoal around cavity	Metals probably present
White infusible mass of oxide, glows strongly on heating	No deposit	Mg, Ca, Sr, Al *
Green infusible mass of oxide	Ditto	Cr
Grey spongy metal mass, attracted by a magnet	Ditto	Fe, Co, Ni
Red spongy metal mass	Ditto	Cu
Bright white malleable bead	Ditto	Ag
Malleable bead, becomes coated with white oxide when removed from flame	Ditto	Sn
Bright malleable bead	Yellow oxide deposit	Pb
Bright brittle bead	Yellow-brown oxide deposit	Bi
Ditto	Blue-edged white oxide deposit	Sb
No bead formed	Oxide deposit, yellow when hot and white when cold	Zn
Ditto	Red-brown oxide deposit	Cd
Ditto	White oxide deposit. An odour of garlic appears (*caution*)	As

* Aluminium can be detected as follows. Moisten the mass in the charcoal cavity with *a few drops* of dilute $Co(NO_3)_2$ and heat again in the blow-pipe flame. *Blue* cobalt aluminate (Thenard's blue, Sec. 53, 10) is formed in the presence of Al. Too much cobalt salt must not be taken, because black cobalt oxide, masking the colour, may be formed.

2. Borax Bead Test. The technique of this test and the chemistry of the processes involved were described in Sec. 54 (pp. 269-270). It should be noted that often the beads formed in the oxidizing and reducing flames differ in colour. Therefore the bead should first be heated in the oxidizing flame (flame zones *1* and *2* in Fig. 50), *its colour examined*, transferred to a reducing flame (*3* and *4* in Fig. 50), and

heated again. The colour should be observed in both cases after the bead has cooled.

Characteristics of various beads are given in Table 31.

Table 31

Borax Bead Colours

Colour (cold) of beads formed in oxidizing flame	Metals probably present	Colour (cold) of beads formed in reducing flame
Blue	Co	Indefinite
Ditto *	Cu	Red-brown
Green	Cr	Green
Brown-yellow or greenish yellow	Fe	Dirty green
Red-brown	Ni	Grey with red or violet tinge
Colourless	Sn	Carmine-red (in presence of traces of Cu) **
Colourless or indefinite	Zn, Ag, Pb, Bi, Cd, Sb	Grey

* With a large amount of copper salt a green bead is formed in the oxidizing flame.

** To test for tin, mix a very small amount (1 : 1,200) of a copper salt with the borax. With large amounts a turbid brown-red bead is formed.

Not only borax, $Na_2B_4O_7 \cdot 10H_2O$, but also microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$ can form coloured beads, but usually the colours of the microcosmic salt beads are less characteristic. It should be used only in testing for chromium, because it gives a green bead with chromium but not with iron, whereas borax gives a green bead with both.

3. Flame Test. Clean the platinum wire to be used in the test by dipping it in HCl and heating strongly, pick up a small amount of the unknown substance on the wire, introduce it into the burner flame, and note the colour. Proceed as follows to ensure that, if the sample is a mixture, its different constituents volatilize separately in accordance with their different volatilities and so interfere as little as possible with each other. First put the wire in the relatively cool region near the base of the flame (*5* in Fig. 50). After some time transfer it to the hottest zone (*6* in Fig. 50). Finally, take the wire out of the flame, moisten it with HCl to convert non-volatile salts into volatile chlorides, and repeat the above procedure.

Different cations give characteristic colours in the flame (Table 32).

Table 32

Flame Tests

Flame colour	Metals probably present	Flame colour	Metals probably present
Yellow (invisible through indigo solution or blue glass)	Na	**Brick-red**	Ca
		Crimson	Sr
		Yellow-green	Ba
		Green	Cu, Bi
Violet (appears purple when viewed through indigo solution)	K	**Sky-blue**	Cu, Pb, As, Sb

It should be remembered that all the preliminary tests described above give distinct results only with pure substances. Conversely, in analysis of mixtures some metals may mask others. Therefore the results of preliminary tests must be interpreted with great caution; on no account should the analysis be confined to preliminary tests only. Every inference must be confirmed by other tests for the particular ions.

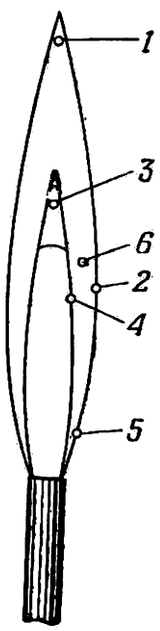


Fig. 50. Structure of the gas burner flame

When the preliminary tests have been completed, the sample is subjected to systematic analysis; one of the portions separated earlier (p. 486) is used for detection of cations, and the other for anions.

If the sample for analysis is a solution free from precipitate, cations of heavy metals must be removed before testing for anions. This operation will be described in detail later (p. 504).

On the other hand, if the substance is a solid or a solution with a precipitate, the first step in the analysis is to dissolve the substance.

112. Detection of Cations

As will be explained more fully later, it is preferable to start analysis with detection of cations, as in the presence of certain cations it may be assumed that some anions must be absent; this facilitates the work. As the analysis is performed mainly in the wet way, the substance to be investigated must first be dissolved.

First we consider how to dissolve substances which do not appear to be metals or alloys.*

A. SAMPLE IS A SOLID

In this case a suitable solvent is found by separate tests with small portions of the substance, the sample is dissolved, and the solution is analyzed for cations. To find a solvent, first test whether the substance is soluble in water (see below, 1). If it does not dissolve in water (or is only partially soluble), test the effect of acids (HCl, HNO_3, and aqua regia, a mixture of these two acids). If the substance does not dissolve in acids either, dissolve and analyze it as described in 3.

1. Dissolving and Analysis of Substances Soluble in Water. A very small amount of the substance is treated in a test tube with a few millilitres of distilled water and heated if necessary. If it does not dissolve completely it is necessary to ascertain whether it is partially soluble. A small portion of the liquid is filtered off from the residue and a few drops of the filtrate are evaporated to dryness in a porcelain basin or on a metal plate. If a deposit remains, the substance is partially soluble.

If the substance is completely soluble in water, about 20 ml of solution is prepared from not more than 0.5-1 g of the substance. Sometimes it is an advantage to take even less, because *the less is taken for analysis the less time is needed for such analytical operations as filtration and washing of precipitates, precipitation by hydrogen sulphide, etc.* Of course, it is not rational to take too little either, because some elements present in small amounts in the substance may be missed. The following rule must be obeyed: never discard portions of precipitates or filtrates obtained in the course of separations, otherwise the amount of substances being analyzed decreases rapidly during the analysis and not enough may be left for detection of certain ions.

If the substance is partially soluble in water, in many cases it is convenient to dissolve all the water-soluble components and to analyze the solution and residue separately. Of course, this may take somewhat longer than if the substance was completely soluble in acid and was analyzed in one stage. However, the analysis is simpler to carry out and the results are more reliable, because the more ions are present in the solution the more do they interfere with each other and the easier it is to make an error.

Extraction of water-soluble components from the mixture, with separate analysis of the solution and insoluble residue, is advan-

---

* Analysis of metals and alloys is discussed in Sec. 115.

tageous also because complications due to the simultaneous presence of oxidizing and reducing agents can sometimes be avoided; this procedure may also give a more correct idea of the true composition of the unknown mixture. For example, if a mixture contains $BaCrO_4$ and KI these two substances are easy to separate, because the first is insoluble and the second is readily soluble. Separate analysis of the solution and the undissolved residue gives a completely correct indication of the composition of the mixture. A different result is obtained if the mixture is dissolved in acid. The following reaction occurs during the dissolving:

$$2BaCrO_4 + 6KI + 16HCl = 2BaCl_2 + 2CrCl_3 + 3I_2 + 6KCl + 8H_2O$$

Therefore, if sufficient KI is present, Cr^{+++} cations will be detected instead of CrO_4^{--} ions, and free I_2 will be found together with I^- ions, i.e., quite erroneous conclusions will be drawn about the composition of the mixture.

Before systematic analysis of the resultant solution, as usual, its colour should be noted and pH determined.

Inferences concerning the presence or absence of coloured ions (Cu^{++}, Co^{++}, Ni^{++}, Fe^{+++}, Cr^{+++}, CrO_4^{--}, $Cr_2O_7^{--}$, MnO_4^-) may be drawn from the colour, and sometimes the presence of some of them may be directly indicated.

Determination of the solution pH also gives certain preliminary indications of the presence of certain ions. The pH determination is performed either directly with a separate portion of the solution (if the substance is completely soluble in water) or after filtration to remove undissolved residue (if the substance is partially soluble in water). If the substance has to be dissolved in acids (see below, 2), then before the pH determination a separate portion of the solution must be cautiously neutralized by alkali until a faint turbidity, which does not vanish on stirring, appears; the turbidity is filtered off and the solution is tested.

An alkaline reaction indicates the presence of free bases or hydrolyzed salts of weak acids and strong bases (such as Na_2CO_3, Na_2S, $Na_2B_4O_7$, CH_3COONa) in the solution.

An acidic reaction may be due to the presence of free acids or acid salts such as $NaHSO_4$ or, most commonly, salts of strong acids and weak bases, such as NH_4Cl, $AlCl_3$, $CuSO_4$, etc.

Finally, if the solution is neutral, it may contain unhydrolyzed salts of strong acids and strong bases, or hydrolyzed salts such as CH_3COONH_4, formed from a weak acid and a weak base of equal strength.

The results of pH *determinations must be regarded as merely tentative. They must be invariably checked and confirmed during analysis by tests for the corresponding ions.* In such cases they are very useful, because they increase confidence in the results or else indicate that an error has been made.

2. Dissolving and Analysis of Substances Insoluble in Water. If the substance is insoluble in water, investigate its solubility in acids. Proceed as follows.

(a) Treat a small portion of the substance in a test tube with dilute (2 *N*) hydrochloric acid. Note whether any gases (CO_2, SO_2, H_2S, NO_2) are evolved, and take this into account in subsequent analysis for anions. If the substance does not dissolve in the cold, heat the mixture. If it does not dissolve completely on heating, remove the dilute acid and replace it by concentrated.

(b) Regardless of the results of the preceding test, heat another portion of the substance with HNO_3 (sp. gr. 1.2).

(c) Finally, if the substance does not dissolve in either hydrochloric or nitric acid separately, test the effect of a mixture of the two (i.e., aqua regia) on heating.

Most substances which are insoluble in water are dissolved by even dilute HCl. Because of its oxidizing properties, nitric acid dissolves a number of substances insoluble in HCl. These include the sulphides of analytical Group IV: CuS, PbS, Bi_2S_3, etc. However, some compounds of bismuth, antimony and tin, insoluble in HNO_3, dissolve in HCl. Aqua regia, which is a stronger oxidizing agent than nitric acid, dissolves some substances which are insoluble in HCl or HNO_3 separately (such as HgS). Nevertheless, some substances do not dissolve even in aqua regia. They are dissolved and investigated as described in 3.

If the substance is soluble in both HCl and HNO_3, in many cases nitric acid is to be preferred, because nitrates are less volatile than chlorides; therefore when excess acid is removed by evaporation there is less risk of losing any of the constituents of the sample.*

Evaporation is necessary, because the precipitation of certain Group IV and V sulphides (especially CdS) is incomplete at high H^+ ion concentrations. Moreover, excess nitric acid or aqua regia is inadmissible also because in precipitation of Groups IV and V they would oxidize hydrogen sulphide to sulphur, thus preventing precipitation of these groups.

At the same time, most of the anions which might interfere with detection of cations are removed from solution (owing to volatili-

---

* For example, hydrochloric acid solutions containing arsenic must not be evaporated because $AsCl_3$ is volatile. Because of the volatility of $HgCl_2$, mercury may also be lost by incautious evaporation.

zation as the corresponding free acids, or to oxidation) during evaporation with acids. This procedure does not remove PO_4^{---} ions, the presence of which is harmful because it results in precipitation of the phosphates of Group II cations and magnesium together with Group III cations during precipitation of the latter by $(NH_4)_2S$. The analysis of cations in the presence of PO_4^{---} is discussed in Sec. 113.*

Most complete removal of NO_3^- ions from solution is achieved by evaporation with a small amount of sulphuric acid until dense white fumes of SO_3 appear. This operation was used in analysis of Group IV cations (p. 373). It should be borne in mind, however, that any Ba^{++}, Sr^{++} and Pb^{++} ions present would be precipitated by sulphuric acid as the sulphates (Ca^{++} may also be partially precipitated), which would complicate the analysis somewhat. Therefore if these ions are present excess nitric acid is removed by simple evaporation to dryness.

In evaporation *strong heating of the dry residue must be carefully avoided*, because many salts would be decomposed with formation of the corresponding oxides which often become insoluble in acids after strong heating. To avoid this, evaporation should preferably be completed on a water bath.

In such cases, the solution for detection of cations is prepared as follows.

Having found a suitable acid solvent as the result of preliminary tests, dissolve about 0.5 g of the substance in the *minimum amount* of this acid. Evaporate the solution *cautiously* to dryness** in a porcelain basin, heat the dry residue with 4-5 ml of 2 *N* HCl, and dilute with 15-20 ml of water. If a precipitate is formed (chlorides of silver, lead, and univalent mercury, and basic salts of bismuth, antimony and tin), filter it off and investigate as described on p. 401 (3-7). Investigate the filtrate according to Table 26 (3-10) and to the corresponding description of the analytical procedure (p. 405).

If the substance was dissolved in HNO_3 or aqua regia, Sn^{++}, Fe^{++} and Hg_2^{++} ions cannot be present in solution; this must be taken into account.

---

* The removal of SiO_3^{--} and F^- ions, which may also interfere in tests for cations, is described in this section, 3.

** Or with sulphuric acid until white fumes of SO_3 appear, if the substance was dissolved in HNO_3 or aqua regia and if the cations Ba^{++}, Sr^{++}, Ca^{++} and Pb^{++}, which form sparingly soluble sulphates, are absent. If the substance is dissolved in HCl, excess acid need not be evaporated; it may be neutralized by ammonia, which is added until the solution is alkaline. HCl (2 *N*) is then added until the solution is faintly acid, followed by more HCl (about 1/5 of the total solution volume). Of course, the test for NH_4^+ must be performed before addition of NH_4OH.

3. Dissolving and Analysis of Substances Insoluble in Acids. Substances insoluble in acids include silver halides*: AgCl, AgBr, AgI; sparingly soluble sulphates**: $BaSO_4$, $SrSO_4$ ($CaSO_4$), $PbSO_4$; the oxides Al_2O_3, Cr_2O_3 and Fe_2O_3 in the native form or produced by strong heating of precipitates, and also SnO_2 and SiO_2. Many silicates, chromite $Fe(CrO_2)_2$, feldspar (CaF_2), sulphur, carbon, and certain other substances also belong to this class.

Methods of dissolving the above-named halides and sulphates have already been discussed.

For example, AgCl dissolves in NH_4OH to form the complex salt $[Ag(NH_3)_2]Cl$, which decomposes when acidified with HNO_3 solution (Sec. 66). AgI and AgBr can be dissolved by the action of a piece of metallic zinc and H_2SO_4 on heating, e.g.,

$$2AgI + Zn + H_2SO_4 = \downarrow 2Ag + ZnSO_4 + 2HI$$

The black precipitate of metallic silver which is formed is dissolved in hot HNO_3 (sp. gr. 1.2) and Ag^+ ions are detected in the solution by their characteristic reactions (Sec. 67).

The anions I^- and Br^- are detected in the solution as described in Sec. 99, 4.

Lead sulphate, $PbSO_4$, dissolves in 30% ammonium acetate solution and in excess of caustic alkalies. The Pb^{++} ion is detected in the resultant solution by the action of K_2CrO_4 (after addition of CH_3COOH if an alkali was used as the solvent). The sulphates of barium, strontium and calcium are dissolved by repeated boiling with concentrated Na_2CO_3 solution and investigated as described on p. 177. They can also be converted into the corresponding carbonates by fusion with a mixture of Na_2CO_3 and K_2CO_3 (Sec. 35, 2).

Silica, SiO_2, and *silicates not decomposed by acids* are dissolved also by fusion of the *finely powdered* substances with approximately six times the amount of $Na_2CO_3 + K_2CO_3$. Soluble sodium and potassium silicates are formed, e.g.,

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2 \uparrow$$

The cooled melt is treated cautiously with dilute HCl, and the solution is evaporated to dryness two or three times with concentrated HCl to convert silicic acid into an insoluble form. The residue after the last evaporation is heated with 1-2 ml of concentrated HCl,

* Silver chloride dissolves in concentrated HCl to form the complex compound $H[AgCl_2]$, but is reprecipitated when the solution is diluted with water.

** Lead sulphate is appreciably soluble in concentrated acids, forming the acid salt $Pb(HSO_4)_2$.

a little water is added, the undissolved silicic acid is filtered off, and the solution is tested for cations in the usual way.

It is obvious that K^+ and Na^+ cannot be detected if this method for decomposing silicates is used, because these cations are introduced in the fusion. Therefore if it is required also to test for K^+ and Na^+ silicates are decomposed by treatment with a mixture of hydrofluoric (HF) and sulphuric acids. This is done in a platinum crucible; a small amount of the finely powdered substance is treated with 2-3 ml of pure hydrofluoric acid and a few drops of concentrated sulphuric acid. The liquid is then evaporated to dryness over a small flame in the fume cupboard, avoiding strong heating. The dry residue is moistened with a little HF and evaporated again. Gaseous silicon fluoride, SiF_4, is formed; as a result, after two or three evaporations with HF the silicate is completely decomposed and silicic acid is removed from the sample. The residue after the last evaporation is dissolved in HCl and the solution is tested for cations.

Insoluble oxides of aluminium and iron, Al_2O_3 and Fe_2O_3, can be brought into solution by fusion with $KHSO_4$, which results in formation of the corresponding sulphates, e.g.,

$$Al_2O_3 + 6KHSO_4 = Al_2(SO_4)_3 + 3K_2SO_4 + 3H_2O$$

The fusion is performed as follows. Mix a small amount of the finely powdered substance with approximately 12 times the amount of $KHSO_4$, put the mixture in a crucible and heat, increasing the temperature gradually, until the mixture ceases to heave and becomes a homogeneous liquid mass. Allow the melt to cool, treat it on warming with a small amount of water, and test the solution for cations*.

Chromic oxide, Cr_2O_3, and *chromite*, $Fe(CrO_2)_2$, can be brought into solution by fusion with approximately six times the amount of a mixture of Na_2CO_3 (2 parts) with $NaNO_3$ or KNO_3 (1 part). Trivalent chromium is oxidized to the sexivalent state:

$$Cr_2O_3 + 2Na_2CO_3 + 3KNO_3 = 2Na_2CrO_4 + 3KNO_2 + 2CO_2 \uparrow$$

The chromate formed can be extracted from the melt with water and detected by tests for the CrO_4^{--} ion (Sec. 54). After this treatment of chromite, iron remains in the residue in the form of an acid-soluble modification of Fe_2O_3.

Tin dioxide SnO_2 and *metaantimonic acid* $HSbO_3$ can be brought into solution by fusion with an approximately sixfold amount of

---

* It should be borne in mind that the amphoteric oxides Al_2O_3 and Cr_2O_3 can also be brought into solution by fusion with Na_2CO_3, being converted into aluminate and chromite. It is preferable to fuse Cr_2O_3 with Na_2CO_3 and $NaNO_3$ as described below.

a mixture of sodium carbonate and sulphur (1 : 1). Water-soluble thiosalts are formed:

$$2SnO_2 + 2Na_2CO_3 + 9S = 2Na_2SnS_3 + 2CO_2 + 3SO_2$$

The fusion should be performed over a small flame in a *fume cupboard* in a covered crucible, continuing the heating until excess sulphur has been evaporated off and burnt. The melt is cooled, treated with warm water, the undissolved residue is filtered off, and the filtrate is tested for antimony and tin (starting with decomposition of thiosalts) in accordance with Table 26 (p. 409).

It should also be noted that freshly precipitated metastannic and metaantimonic ($HSbO_3$) acids, formed, for example, when alloys are dissolved in HNO_3, are appreciably soluble in hot concentrated HCl; this is convenient to use for detection of tin and antimony in alloys.

Insoluble fluorides, such as CaF_2, are detected by the test of SiF_4 formation (Sec. 94, 4). Insoluble fluorides can also be decomposed by heating with concentrated H_2SO_4 in a platinum crucible. The heating is continued (*in a fume cupboard*) until the H_2SO_4 has been evaporated almost to dryness. Free HF, which volatilizes on heating, is displaced from the fluoride while the residue contains the corresponding sulphate, such as $CaSO_4$, which is dissolved and investigated by the usual methods.

Carbon is detected by its black colour and by combustion when fused with a mixture of Na_2CO_3 and $NaNO_3$ with formation of CO_2 which turns a drop of lime water cloudy.

Sulphur is identified by the blue colour of the flame when it burns, with formation of SO_2 (*recognized by its smell*); it is also detected by its ability to sublime when the sample is heated in a narrow tube sealed at one end*.

B. SAMPLE IS A SOLUTION WITH A PRECIPITATE

In this case the precipitate is filtered off and its solubility in acids is investigated. All the constituents of the sample which are dissolved by acids (after removal of excess acid by evaporation and addition of water) are added to the rest of the solution, which is analyzed for cations in the usual manner**. The insoluble residue is decomposed and investigated as described above (p. 495).

---

* It should be remembered that sulphur may be formed when some substances are treated with acids, owing to decomposition of thiosulphates or oxidation of sulphides.

** Alternatively, as indicated in 1 (p. 491) the solutions can be analyzed separately. If the sample is a solution without a precipitate it is tested for cations as indicated in Table 26.

113. Detection of Cations in Presence of the Phosphate Anion

It has already been said that the presence of phosphate ions in solution interferes with separation of Group III cations from Groups II and I. The reason is that, being insoluble in water but soluble in acids, the phosphates of Group II cations and magnesium must be precipitated if the acid reaction of the solution changes to alkaline or neutral. This is precisely what happens in precipitations of Group III cations by ammonium sulphide in alkaline solution (Sec. 52). It is therefore clear that in the presence of phosphates Group III cations cannot be separated from Group II by the action of $(NH_4)_2S$. Group II cations, together with Mg^{++}, may be precipitated completely or partially (in accordance with the amount of PO_4^{---} present). Therefore phosphate ions must be removed in order to achieve separation.

Phosphate ions may be removed by various methods, such as precipitation of PO_4^{---} by $SnCl_4$ or ZrO_2Cl_2 in hydrochloric acid solution, by Bi^{+++} ions in nitric acid solution, or by Fe^{+++} ions in the presence of acetate buffer, etc. Here only this last method is considered in detail. It is based on the fact that in the presence of CH_3COOH + + CH_3COONH_4 buffer mixture, which gives a pH value of about 5 in the solution, the PO_4^{---} ion can be completely precipitated as $FePO_4$. At this pH, Ba^{++}, Sr^{++}, Ca^{++} and Mg^{++} ions, as well as Zn^{++}, Mn^{++}, Ni^{++}, Co^{++} and Fe^{++}, remain in solution. On the other hand, the phosphates of aluminium and chromium may be precipitated together with $FePO_4$. Addition of excess Fe^{+++} ions interferes with complete precipitation, as the $FePO_4$ precipitate is dissolved owing to formation of a complex. The solution is boiled to remove Fe^{+++} ions and to ensure complete precipitation of PO_4^{---}. Excess Fe^{+++} ions are then precipitated as the basic acetate, $CH_3COO(OH)_2Fe$. The basic acetates of aluminium and chromium (if any ions of these elements still remained in solution) may be precipitated with it.

The precipitate of phosphates and basic acetates formed during precipitation of PO_4^{---} is investigated for Al^{+++} and Cr^{+++}, and the solution is tested for Groups III, II, and I.

If the solution being analyzed may contain cations of all five analytical groups together with phosphate ions, Groups IV and V are separated and analyzed in the usual way (p. 409). The solution remaining after the separation, containing cations of Groups III, II and I, is investigated as described below. The analytical procedure is given schematically in Table 33 (p. 501).

ANALYSIS OF CATIONS OF GROUPS III, II AND I IN PRESENCE OF PHOSPHATE IONS

1. Preliminary Tests and Oxidation of Fe^{++}. Evaporate the filtrate after separation of Groups IV and V by hydrogen sulphide to about

15-20 ml to remove H_2S, filter off the precipitated sulphur, and heat for a few minutes with 1-2 ml of H_2O_2 solution to oxidize Fe^{++} to Fe^{+++}. Test separate portions of this solution for the following ions:

(a) PO_4^{---} by the action of ammonium molybdate* or by the spot test with $(NH_4)_2MoO_4$ and benzidine in the presence of tartaric acid (Sec 92, 5);

(b) Fe^{+++} by the action of $K_4[Fe(CN)_6]$ in the presence of HCl**;

(c) NH_4^+ by the usual tests.

If phosphate is present, proceed as described in 2. In the absence of phosphate analyze the solution in accordance with Sec. 60.

2. Separation of PO_4^{---}. Add NH_4OH drop by drop to the whole solution until a permanent turbidity (due to phosphates and hydroxides) appears, or until alkaline to litmus if no turbidity forms***. Then add 2 *N* HCl drop by drop until the precipitate dissolves, or until the solution is acid to litmus (*avoid an excess of* HCl).

Add 30% CH_3COONH_4 solution to the weakly acidic solution****, and check the solution pH.

Bring the pH to about 5 by addition of HCl or CH_3COONH_4. If Fe^{+++} ions are present in excess of the amount required to precipitate all the PO_4^{---} in solution, the solution turns a red-brown colour. If it does not turn red, add $FeCl_3$ solution drop by drop until this colour appears. Then dilute the solution, together with the precipitate, with water and boil for 2-3 minutes to precipitate excess Fe^{+++}. Filter rapidly while hot***** and wash the precipitate.

Investigate the precipitate of phosphates and basic acetates (of aluminium, chromium, and iron) as described in 3, and the filtrate according to 4.

---

* For the ammonium molybdate test, boil 0.5-1 ml of the solution with 1-2 ml of HNO_3 (sp. gr. 1.2) and add it drop by drop to four or five times its own volume of the reagent heated to 40-50°. If no precipitate forms, leave to stand. It is useful to add a little solid NH_4NO_3.

** Tests (b) and (c) are carried out if the presence of iron and ammonium ions has not been established before precipitation of Groups IV and V by hydrogen sulphide (see p. 404, 1, B).

*** If no precipitate (turbidity) appears on addition of ammonia until alkaline, Group II cations and Mg^{++} must be absent. Group III cations cannot be present either, except Zn^{++}, Co^{++}, and Ni^{++}, the phosphates of which are readily soluble in NH_4OH and may not be precipitated.

**** When excess CH_3COONH_4 is added to a solution containing free HCl, the equivalent amount of CH_3COOH is formed. An acetate buffer mixture, required in the separation of PO_4^{---} ions, is thus produced in the solution. Excess HCl should be avoided because it makes precipitation of PO_4^{---} incomplete.

***** The solution must not be allowed to cool because the equilibrium of ferric acetate hydrolysis

$$Fe^{+++} + 3CH_3COO^- + 2H_2O \rightleftarrows \downarrow CH_3COO(OH)_2Fe + 2CH_3COOH$$

shifts to the left, i.e., towards formation of Fe^{+++} ions, on cooling. In the presence of these ions precipitation of PO_4^{---} becomes incomplete.

3. Detection of Al^{+++} and Cr^{+++} Ions. Dissolve the precipitate on the filter in hot 2 *N* H_2SO_4. Add concentrated (25%) NaOH to the solution until alkaline. Then add excess alkali (about $^1/_4$ of the total volume) and a few millilitres of 3% H_2O_2 and boil the liquid for a few minutes. Cr^{+++} is then oxidized to CrO_4^{--} ions, which pass into solution together with AlO_2^- ions and excess NaOH, while iron is precipitated as $FePO_4$ and $Fe(OH)_3$.

As Fe^{+++} has already been tested for, filter off and reject the precipitate.

Test separate portions of the filtrate for CrO_4^{--} and Al^{+++} ions as described for analysis of Group III cations (pp. 307-308, 8-10).

4. Detection of Cations of Groups III, II and I. The filtrate obtained in 2 may contain the remaining Group III cations together with Groups II and I.

As PO_4^{---} has been removed, this filtrate is analyzed in the usual way (p. 303).

Other Methods for Separation of Phosphate. **1. Separation of PO_4^{---} by the action of $SnCl_4$** is based on formation of an adsorption compound of phosphate with the stannic acid formed by hydrolysis of $SnCl_4$ at a definite pH value. To prepare the reagent, shake 1 g of $SnCl_4 \cdot 3H_2O$ with 1 ml of water at room temperature.

The procedure for removing PO_4^{---} ions by this method is as follows. Boil out H_2S from the solution, add 8-10 drops of $(NH_4)_2HPO_4$ solution to raise the PO_4^{---} ion concentration*, and then add ammonia drop by drop until the precipitate which forms begins to dissolve slowly. Then add two drops of 2 *N* HCl and dilute with water to 10 ml. Having thus adjusted the acidity, heat the solution to boiling and add 10-12 drops of the reagent solution, a drop at a time with stirring. $SnCl_4$ is hydrolyzed and forms a precipitate of stannic acid, which adsorbs phosphate ions from the solution.

Filter off the precipitate and test a portion of the filtrate with ammonium molybdate for complete precipitation of PO_4^{---}. If phosphate is still present in the solution, repeat the precipitation adding more reagent. When the precipitation is complete, filter off and discard the precipitate. Pass hydrogen sulphide through the filtrate to remove excess Sn^{++++} ions in the form of SnS_2; first adjust the acidity in the usual way (see p. 404,4). When the precipitation is complete, filter off and discard the precipitated SnS_2, boil the filtrate to remove H_2S, concentrate it by evaporation, and analyze for Groups III, II and I according to Table 18 (p. 309) or Table 19 (p. 314).

2. Separation of PO_4^{---} in the form of $BiPO_4$ is based on the fact that bismuth phosphate is almost insoluble in dilute (0.5 *N*) HNO_3. However, it is much more soluble in hydrochloric acid, and therefore the solution must be free from Cl^- ions. They can be removed by evaporating the solution twice with HNO_3 almost to dryness.

The separation of PO_4^{---} by this method is effected as follows. Put the solution into a crucible (or basin) and evaporate to a small volume. Add 0.5-1 ml of 6 *N* HNO_3 and evaporate the solution *almost* to dryness (do not heat strongly). Add a few more drops of HNO_3 and repeat the evaporation. Then add several millilitres of water, transfer the contents of the crucible to a beaker, and dilute to about 10 ml. Neutralize with ammonia against litmus and add

* At low PO_4^{---} concentrations the precipitate is difficult to filter off.

HNO_3 drop by drop with stirring until the last drop produces an acid reaction. Then add the calculated amount of acid to make the acid concentration in the solution approximately 0.5 *N**. Dilute the solution to 15 ml, heat, and precipitate PO_4^{---} by adding 0.1 *M* $Bi(NO_3)_3$ solution in portions of five drops until precipitation is complete. Add a small excess of bismuth nitrate, heat the contents of the beaker for several minutes (to coagulate the precipitate),

Table 33

Analysis of Mixtures of Groups III-I Cations in Presence of Phosphate

1. Boil out H_2S, oxidize Fe^{++} to Fe^{+++} by H_2O_2. Preliminary tests: test for PO_4^{---}, Fe^{+++} and NH_4^+ (in separate portions of the solution)
2. Remove PO_4^{---} by action of $FeCl_3$ after neutralizing the solution with NH_4OH and adding CH_3COONH_4 to the weakly acidic solution (to pH≈ ≈5). Boil to precipitate excess Fe^{+++} in the form of $CH_3COO(OH)_2Fe$

Precipitate: $FePO_4$, $AlPO_4$, $CrPO_4$ and basic acetates of iron, aluminium and chromium 3. Dissolve precipitate in H_2SO_4. Separate Fe^{+++} from Al^{+++} and Cr^{+++} by the action of excess NaOH and H_2O_2	*Filtrate:* remaining Group III cations together with Groups II and I 4. Analyze the solution for cations of Groups III, II and I (see Table 18, p. 309)
Precipitate: $FePO_4$, $Fe(OH)_3$. Not investigated	*Filtrate:* AlO_2^-, CrO_4^{--} (NaOH). Test for CrO_4^{--} and Al^{+++}

filter, and check again for complete precipitation. If the precipitation is complete, transfer the filtrate to another beaker and precipitate excess Bi^{+++} ions by H_2S. When the precipitation is complete, filter off and discard the precipitated Bi_2S_3. Boil out H_2S from the filtrate, evaporate it down to 5 ml, and analyze for Groups III, II and I according to Table 18 (p. 309) or Table 19 (p. 314).

3. Separation of PO_4^{---} by precipitation with $Zr(NO_3)_4$ solution is based on the fact that zirconium phosphate, $Zr(HPO_4)_2$, is almost insoluble in 0.3 *N* HCl, while excess Zr^{++++} can be removed by means of ammonia.

The PO_4^{---} ion is precipitated as follows. First boil out H_2S from the filtrate after separation of Groups IV and V and add a little solid NH_4Cl. Then add 2-3 ml of $Zr(NO_3)_4$ solution** drop by drop, stirring thoroughly with a glass rod, followed by ammonia until alkaline to litmus.

Heat the contents of the test tube for about 5 minutes on a water bath and then acidify the solution with 2 *N* HCl.

Add the acid drop by drop until the solution is acid to litmus, followed by an excess corresponding to 1 ml of HCl per 10 ml of solution. Heat the test tube again on the water bath to dissolve Group III hydroxides. The residue

* Calculate from the normality of the HNO_3 for a total volume of 15 ml of the solution for precipitation.

** This solution should contain 50 mg of zirconium nitrate in 1 ml.

contains $Zr(HPO_4)_2$ and metazirconic acid, H_2ZrO_3. It is formed when zirconium hydroxide (precipitated by ammonia) is heated, and is almost insoluble in dilute HCl.

Filter off and discard the precipitate. Evaporate a small portion of the filtrate to dryness with HNO_3, dissolve the dry residue in 1-2 ml of HNO_3, and test the solution for PO_4^{---} by means of ammonium molybdate on heating. If the precipitation is incomplete, add some more $Zr(NO_3)_4$ to the solution and repeat the above operations.

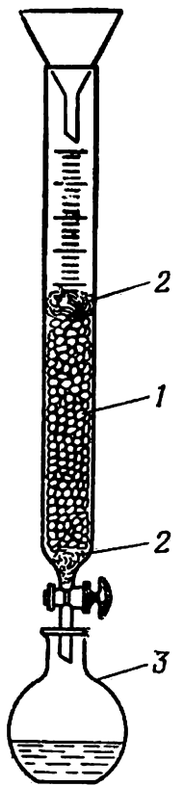


Fig. 51. Apparatus for chromatographic separation of PO_4^{---} ions
1 — cation exchange resin; 2—glass-wool plugs; 3—flask for collecting the solution

When the precipitation is complete, separate off the precipitate and analyze the solution for Groups III, II, and I.

The precipitation of Zr^{++++} as H_2ZrO_3 is incomplete, and a small amount of zirconium passes into solution. Zirconium is completely precipitated during subsequent separation of Group III by the action of $(NH_4)_2S$ in ammoniacal solution. When Group III is separated into its subgroups, zirconium is found in the precipitate together with ferric, aluminium, and chromic hydroxides. During the subsequent treatment of the precipitate with excess NaOH and H_2O_2 a very small amount of zirconium may be dissolved together with CrO_4^{--} and AlO_2^- ions. The presence of zirconium need be taken into account only in detection of Al^{+++}, as after the solution has been acidified and ammonia added zirconium hydroxide, resembling the aluminium hydroxide precipitate, is precipitated together with $Al(OH)_3$.

To avoid error, before adding ammonia to the solution the acidity of the latter should be the same as in the precipitation of PO_4^{---} (i.e., the excess of 2 *N* acid should be 1 ml per 10 ml of solution). Then add 5-6 drops of Na_2HPO_4 solution and heat for 3-5 minutes. If a precipitate of $Zr(HPO_4)_2$ is formed filter it off and discard, and add ammonia to the filtrate until alkaline to precipitate Al^{+++}.

In addition to the methods described above, PO_4^{---} can also be precipitated in the form of lead or titanium phosphate.

4. Chromatographic method. Chromatographic separation of PO_4^{---} and other interfering anions is based on sorption of all the cations present in the solution when it is passed through a column containing a cation exchanger in the hydrogen form. All the anions (including PO_4^{---} ions) remain in solution in the form of the corresponding free acids. The column is washed out with water, the sorbed cations are displaced by the action of HCl solution, and after complete elution the resultant solution of chlorides together with the washings is analyzed for cations. A description of this method as recommended by I. G. Lakomkin is given below.

a. Preparation of the cation exchanger for the determination. An ordinary 25-ml burette with a glass tap is used (Fig. 51). Put a small plug of glass wool in the constriction of the burette above the tap, and cover it with 10 g of the cation exchanger, previously kept in water for at least 24 hours. Cation-exchange resin of the СБС grade is used. Put a glass-wool plug on top of the resin. The resin must be prepared before the experiment. To do this, pass 15-20 ml of 6 *N* HCl solution through the resin in the burette in order to replace any cations which may be present by H^+ ions. The acid solution should flow out of the

burette at a rate not exceeding one or two drops per second. When not more than 1 ml of acid solution remains above the resin in the burette, wash the resin with water until a drop of the washings no longer produces a pink colour on a piece of paper soaked in methyl orange (i.e., until the pH of the washings reaches the value of about 4).

b. Sorption of cations, and separation from PO_4^{---} and other anions. Find the pH of the solution to be tested. It should not be less than 1.5-2. If the acidity is higher, evaporate it *cautiously* almost to dryness (do not heat strongly), neutralize with ammonia until turbid, dissolve the turbidity in 1-2 drops of 6 *N* HCl, and dilute with water to 10 ml. Pass this solution at the same rate (one or two drops per second) through the resin, which takes up the cations present in the solution and releases the equivalent amount of H^+ ions. To remove the solution containing H_3PO_4 and other acids impregnating the resin, wash the column out thoroughly again (until the pH of the washings reaches ~4).

c. Isolation of the sorbed cations and regeneration of the resin. When the washing is complete, put a clean flask or beaker under the burette and pass 15-20 ml of 6 *N* hydrochloric acid at the same rate as before. Then wash the column out with water to remove the displaced cations, and collect the washings in the same vessel. When the total volume has reached 40-50 ml, transfer the liquid to a porcelain basin and evaporate to dryness on a water bath. Moisten the dry residue with 1-2 drops of 6 *N* HCl, dilute with water to the original volume, and analyze for cations in the usual way. The resin can be used for further determinations.

It follows from the above description that practical separation of cations by this method is somewhat difficult because the column has to be washed out three times followed by evaporation of the solution.

114. Detection of Anions

As already stated, the tests for anions should be carried out only after analysis for cations. This procedure is preferable for the following reasons.

1. The presence or absence of certain anions is established concurrently with the detection of cations. For example, phosphate is detected before precipitation of Group III cations by ammonium sulphide (Sec. 113). If arsenic is absent, the solution cannot contain AsO_3^{---} or AsO_4^{---} anions. Further, if chromium is not found in the solution it can be assumed that CrO_4^{--} and $Cr_2O_7^{-}$ anions must be absent, because these anions are reduced by hydrogen sulphide to Cr^{+++} ions during analysis for cations, and are therefore to be found in cation Group III.

Finally, the presence of S^{--}, SO_3^{--}, $S_2O_3^{--}$, CO_3^{--} and NO_2^{-} anions is usually established in the course of analysis for cations from the liberation of H_2S, SO_2, CO_2 and NO_2 when the solution is acidified.

2. Some valuable inferences concerning the absence of various anions can also be drawn from the solubilities of the salts of the metals found to be present. Suppose, for example, that cations forming sparingly soluble salts with anions such as S^{--}, CO_3^{--}, PO_4^{---}, etc., have been found in the substance. If the substance is soluble in water, these anions cannot be present. If Ba^{++}, Sr^{++}

or Pb^{++} are present and the substance dissolves in dilute HCl or HNO_3, SO_4^{--} cannot be present. If the unknown solution (provided that it does not contain a precipitate) is found to contain Ag^+, it may be concluded that Group II anions are absent. If, moreover, the solution is not acid it cannot contain any Group I anions except SO_4^{--} and F^-, because their silver salts (apart from silver sulphate and silver fluoride) are sparingly soluble in water.

Having made such inferences concerning the absence of certain anions, proceed to detect those which may be present.

First, the solution must be suitably prepared; if the unknown substance is a solid, it must be dissolved. It must be remembered that the solution used in analysis for cations must not contain cations of Groups II-V or Mg^{++}. Many of these cations are coloured, or have oxidizing or reducing properties, or form precipitates with a number of anions. All this interferes with detection of anions.

To remove cations of Groups II-V and Mg^{++}, boil the sample with Na_2CO_3 solution. The anions present in the sample remain in solution (or are dissolved if the sample is a solid) as the corresponding sodium salts, while cations of Groups II-V and Mg^{++} are precipitated (or remain in the residue) as neutral or basic carbonates, or in some instances as hydroxides, e.g.,

$$BaSO_3 + Na_2CO_3 = \downarrow BaCO_3 + Na_2SO_3$$

$$2CuSO_4 + 2Na_2CO_3 + H_2O = \downarrow (CuOH)_2CO_3 + 2Na_2SO_4 + CO_2\uparrow$$

$$2AlCl_3 + 3Na_2CO_3 + 3H_2O = \downarrow 2Al(OH)_3 + 6NaCl + 3CO_2\uparrow$$

The resultant solution, described as the "prepared solution" is used for detection of anions.

It should be borne in mind, however, that certain substances are difficult to decompose by boiling with sodium carbonate. They include, for example, certain phosphates, fluorides and sulphides, and also silver halides. Therefore, if the corresponding anions are not found in the prepared solution, they should be tested for in the precipitate formed by the action of Na_2CO_3, or, in certain instances, in separate portions of the original solid.

Of course, if the only cations present are K^+, Na^+ or NH_4^+ special preparation of the solution is not necessary. In this case simply dissolve about 0.5 g of the substance in 15-20 ml of distilled water and test separate portions of this solution for anions as described on p. 476 et seq.

If cations of Groups II and V or Mg^{++} are present and special preparation of the solution becomes necessary, *a test for* CO_3^{--} *must be carried out with a separate portion of the substance.*

The prepared solution is made as follows.

(a) If the substance is a solid, mix about 0.5 g of it, finely powdered, in a small beaker (or basin) with 2-3 g of pure anhydrous sodium carbonate (Na_2CO_3), add 15-20 ml of distilled water, and heat while stirring with a glass rod. Bring the liquid to the boil, and boil gently for about 5 minutes, adding water to make up for evaporation. Filter off the precipitate and keep it for testing for certain undissolved anions (see below).

(b) If the substance is a solution (or a solution with a precipitate), neutralize 15-20 ml by Na_2CO_3 solution, add 2-3 g of anhydrous sodium carbonate, and proceed as described above (a).

(c) If the substance is dissolved (for detection of cations) by fusion with a mixture of Na_2CO_3 and K_2CO_3 (Sec. 112, 3), use the solution formed when the melt is treated with water for the tests for anions.

Before the prepared solution is analyzed for anions, it should be neutralized with acetic acid to remove excess sodium carbonate. Part of the prepared solution is neutralized with nitric or sulphuric acid so that the CH_3COO^- ion can also be detected.

Perform the neutralization very cautiously, stirring the liquid thoroughly after addition of each portion of acid and *avoiding carefully an excess of acid*; otherwise certain anions (such as S^{--}, NO_2^-, etc.) may be lost. Moreover, it should be borne in mind that some cations are precipitated incompletely on boiling with Na_2CO_3. For example, cations forming amphoteric oxides may partially pass into the prepared solution as the corresponding anions (e.g., AlO_2^-). The copper ion forms a complex compound and also partially remains in solution, colouring it bluish, etc. If the subsequent neutralization is performed accurately, all these compounds are decomposed and the corresponding cations are precipitated, e.g.,

$$NaAlO_2 + CH_3COOH + H_2O = \downarrow Al(OH)_3 + CH_3COONa$$

Similarly, copper is precipitated as the basic carbonate,* $(CuOH)_2CO_3$, etc.

On the other hand, if the neutralization is inaccurate the precipitates formed redissolve partially or completely in the acid, and the object of the whole operation is not achieved. If a precipitate forms during neutralization of the prepared solution, it is filtered off and discarded, and the filtrate is analyzed for anions in the usual way (p. 478 et seq.).

As already stated, certain anions (PO_4^{---}, F^-, S^{--}, Br^- and I^-) may remain undissolved by the action of Na_2CO_3. Therefore, if these anions are not found in the prepared solution, the residue must be tested for their presence.

---

* The copper ion can also be precipitated by boiling the solution with a few drops of caustic alkali solution.

This is done as follows.

(a) Treat a part of the residue with HNO_3 (sp. gr. 1.2) on heating; filter off any undissolved residue, wash, and test for I^- and Br^- by the action of chlorine water (after heating with Zn and H_2SO_4 and removing precipitated Ag). If not found previously, test the filtrate for PO_4^{---}.

(b) Test another portion of the residue for presence of S^{--} by the action of dilute H_2SO_4 and metallic zinc* (Sec. 100, 2). Blackening of paper moistened with $(CH_3COO)_2Pb$ or Na_2PbO_2 solution indicates the presence of S^{--}.

(c) Dry a portion of the residue and test it for the presence of F^- ions by the reaction of SiF_4 formation (Sec. 94, 4). In the absence of borates a separate portion of the original (solid) substance may also be used for this test.

Finally, in the absence of PO_4^{---} the F^- ion can be detected by the zircon-alizarin reaction (Sec. 94, 5) in a portion of the residue dissolved in dilute HCl.

115. Analysis of Metals and Alloys

Finally, let us consider the case when the sample for analysis is a "technically pure" metal or alloy. The purity of a technically pure metal is usually 95-97%, and may reach 99.99%. It is evident that the contents of different impurities (which may be more than 10 in number) must be low, in some cases only thousandths of 1%. Detection of such small amounts (traces) of impurities is sometimes a very difficult problem, requiring more sensitive methods of investigation, such as spectral analysis, etc.

Alloys consist of two or several components. These components dissolve in each other in the molten state, and on cooling they form mechanical mixtures, or *solid solutions*, or chemical compounds with each other. The contents of individual components in alloys are usually not below some tenths of 1%, more often, several per cent.

Many different metals and alloys are used in technology. The most important alloys are divided into four types (Table 34).**

The effects of solvents, which are in most cases determined by the properties of the main alloy component, on alloys are particularly important.

(a) *Iron alloys*, like iron itself, which is to the left of hydrogen in the potential series, usually dissolve in dilute and concentrated

---

* First test the zinc to ensure absence of sulphide as an impurity.

** Of course, the types of alloys given in Table 34 do not cover all the alloys which often have to be analyzed. Only the commonest and most important alloys are included.

HCl and in dilute H_2SO_4 and HNO_3. Concentrated nitric acid often renders iron and its alloys "passive". The metal becomes coated with a thin oxide film which protects it from contact with the acid and greatly retards dissolution. Certain other oxidizing agents act similarly on metals. It must be remembered, however, that certain iron alloys can be dissolved only by boiling with aqua regia or other mixtures of acids, and in some cases only by fusion with fluxing agents* such as Na_2O_2 or NaOH.

Oxidizing agents such as HNO_3, $(NH_4)_2S_2O_8$, etc., also have to be used if the alloy dissolves in dilute HCl or H_2SO_4 but leaves a residue of the carbides (carbon compounds) of certain metals (Cr, W, V, Mo, etc.), which must be oxidized to dissolve them. In such cases the oxidizing agent should be added only after the metal has dissolved (as indicated by the fact that evolution of hydrogen ceases). Otherwise the iron will be rendered passive by the oxidizing agent and will dissolve slowly or not at all.

(b) *Copper alloys*, like copper itself (to the right of hydrogen in the potential series), are insoluble in dilute HCl and H_2SO_4. On the other hand, they dissolve readily in concentrated and dilute HNO_3 (on heating in the latter case). The reaction of dilute HNO_3 with copper can be represented by the equation

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO\uparrow$$

With concentrated HNO_3, NO_2 is evolved instead of NO:

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2\uparrow$$

When tin and antimony are dissolved in nitric acid (of high enough concentration) they form β-stannic acid, H_2SnO_3,** and metaantimonic acid, $HSbO_3$, in the form of white precipitates:

$$3Sn + 4HNO_3 + H_2O = \downarrow 3H_2SnO_3 + 4NO\uparrow$$

or

$$Sn + 4HNO_3 = \downarrow H_2SnO_3 + H_2O + 4NO_2\uparrow$$

These precipitates are appreciably soluble in hot concentrated HCl; this fact can be used for detecting tin and antimony in them.

(c) *Alloys of aluminium and magnesium* are readily soluble in acids. Moreover, aluminium alloys, like aluminium itself, are easily soluble in caustic alkalies, which are the most suitable solvents for them. The reaction between aluminium and caustic alkali

---

* The fusion is performed in an iron or nickel crucible; the crucible material is also partially dissolved. The melt is dissolved in H_2SO_4 and analyzed by the usual methods (see below).

** More accurately, $(H_2SnO_3)_5$; see the footnote on p. 399.

Table 34

Composition and Properties of the Most Important Types of Alloys

Alloy type	Name	Based on	Composition	Colour	Sp. gr.	Solvent
Iron alloys (ferrous alloys)	Cast iron, steels, ferro-alloys, certain superhard alloys	Iron	Fe, Mn, Ni, Cr, V, Co, Mo, Cu, W, Ti (C, P, Si, S)	Dark grey (steely), sometimes nearly black	About 8	H_2SO_4, HCl, $HCl + HNO_3$, etc.
Copper alloys (non-ferrous alloys)	Bronzes, brasses, cupronickel, nickel silver	Copper	Cu, Sn, Cd, Sb, Zn, Pb, Al, Mn, Fe, Ni (P)	Golden, yellow, or silvery white	7-9	HNO_3
Aluminium and magnesium alloys (light alloys)	Duralumin, magnalium, etc.	Aluminium, magnesium	Al, Mg, Ca, Cu, Mn, Ni, Fe, Zn, Sn (Cd, Si)	Silvery white	1.8-2.7	NaOH, HCl, H_2SO_4
Lead alloys (heavy alloys)	Babbitts, solders, type metal, etc.	Lead, tin	Pb, Sn, Cu, Fe, Cd, Zn, Sb (Ca, Na)	Grey, bluish grey, silvery white	8.5-11.5	HNO_3

is represented by the equation

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2 \uparrow$$

Zinc, tin (and silicon) dissolve in alkali in addition to aluminium. The other alloy components remain in the residue as the free metals (or partially as hydroxides) after alkali treatment. Because of the possible presence of copper, this residue should be dissolved in HNO_3.

(d) *Alloys of lead and tin.* Although lead is to the left of hydrogen in the potential series, it is not easily soluble in dilute HCl and H_2SO_4, because the sparingly soluble salts formed ($PbCl_2$ and $PbSO_4$) are deposited on the metal surface and protect it against further action by the acid. Therefore HNO_3 should be used (with heating) for dissolving lead and tin alloys. Any Sn and Sb in the alloy are precipitated in the form of H_2SnO_3 and $HSbO_3$.

Table 35

Preliminary Tests for Determining Alloy Types

1. Treat a granule of the alloy in the cold with concentrated (25%) NaOH. Abundant evolution of hydrogen (effervescence), usually after 1-5 minutes, indicates an aluminium alloy. *	
2. Heat another granule of the alloy with a few drops of concentrated HCl for 1 minute. While still heating, add a drop of HNO_3 (sp. gr. 1.2) to oxidize Fe^{++} to Fe^{+++}. After a minute add NH_4CNS to the solution. An *intense* blood-red colour indicates an iron alloy.	
3. Heat 1-2 granules of the alloy with a few drops of HNO_3 (sp. gr. 1.2) and an equal volume of water. If a precipitate (H_2SnO_3 or $HSbO_3$) forms, filter. Carry out tests 4 and 5 on separate portions of the filtrate.	
4. A blue solution indicates the presence of copper in the alloy. To confirm, add excess concentrated NH_4OH to a portion of the solution. An *intense* blue colour should appear owing to formation of the $[Cu(NH_3)_4]^{++}$ ion.	5. Dilute another portion with water to 2-3 times the initial volume and add a little 2 *N* H_2SO_4. An *abundant* white precipitate of $PbSO_4$ indicates a lead alloy. **

* If external signs (colour, specific gravity) suggest that the alloy is of the light type (aluminium-magnesium alloy), but the alloy does not react with NaOH, treat a granule with cold 2 *N* CH_3COOH. Abundant evolution of hydrogen suggests that the alloy is based on magnesium. In that case dissolve 0.5 g in dilute HCl and analyze the solution in the usual way for cations which might be present in a light alloy (see Table 34).

** An *abundant* white precipitate of H_2SnO_3 when the alloy is treated with HNO_3 according to 3 indicates the presence of large amounts of tin (in tin alloys). Such alloys should be dissolved in dilute (1 : 1) HCl rather than in HNO_3.

Since an alloy of any given type can contain only certain metals characteristic of that type, to simplify analysis one should first determine the type to which the alloy belongs, and then conduct the analysis accordingly. In addition to observations of the physical properties of alloys indicated in Table 34 (colour, specific gravity*), it is useful to carry out certain preliminary tests (Table 35). When performing these tests, *it is necessary to note the intensity of the colour or the amount of precipitate formed.*

For example, it follows from Table 34 that iron is present in many alloys in addition to the ferrous type. However, while in the case of iron-based alloys a very intense blood-red colour is produced by the action of NH_4CNS, in analysis of other alloys the colour is very much weaker, pale reddish. Similarly, a precipitate of $PbSO_4$ may be obtained from a copper alloy, but it is much more abundant in the case of lead alloys, etc.

Table 36

Analysis of Iron and Its Alloys

1. Dissolving. Heat about 0.5 g of the alloy with H_2SO_4 until no more hydrogen is evolved. If a dark-grey or black precipitate of carbides of chromium, tungsten, molybdenum or other metals appears, add a little concentrated HNO_3 and continue heating until the black specks disappear completely.* If an orange or white residue remains, filter it off and wash it with water acidified with HCl.

Precipitate: H_2WO_4 (H_2SiO_3)	*Filtrate*: Fe^{+++}, Cr^{+++}, Mn^{++}, Ni^{++}, Co^{++}, Cu^{++}, Ti^{++++}, VO_3^-, MoO_4^{--}
2. Test for W (p. 424, 2)	3. Test for Group III cations and the ions** Cu^{++}, Ti^{++++}, MoO_4^{--}, and VO_3^- as described in Table 27 (4-9) after first removing excess HNO_3 by evaporation*** with H_2SO_4 until white fumes of SO_3 appear.

* In some cases boiling with aqua regia or even fusion may be necessary to dissolve iron alloys. If aqua regia is used, the subsequent analysis is carried out similarly. Fusion is not considered in this book.

** If it is known that the elements Ti, V, Mo and W cannot be present in the alloy, proceed with the analysis as indicated in Table 27 and on p. 424, omitting the operations for detection of WO_4^{--}, MoO_4^{--}, VO_3^- and Ti^{++++}. It is then also unnecessary to add $(NH_4)_2S_2O_8$ before precipitation with hydrogen sulphide according to 3.

*** Excess HNO_3 (or aqua regia) must be removed before precipitation with hydrogen sulphide.

* This does not imply quantitative determination, but merely a qualitative assessment of specific gravity so that, for example, light and heavy alloys can be distinguished.

Analysis of Copper and Its Alloys

1. Dissolving. Add HNO_3 (sp. gr. 1.2) to about 0.5 g of the alloy by small portions and warm gently. A little solid NH_4NO_3 should be added for better coagulation of H_2SnO_3 and $HSbO_3$. Heat in fume cupboard until the alloy has been completely decomposed. Filter off any residue and wash it with hot water containing NH_4Cl

Precipitate: H_2SnO_3, $HSbO_3$	*Filtrate*: Cu^{++}, Pb^{++}, Cd^{++}, Al^{+++}, Fe^{+++}, Mn^{++}, Ni^{++}, Zn^{++} (HNO_3)

2. Tests for Sn and Sb. Heat the precipitate for a few minutes with concentrated HCl. Filter if necessary; test the solution for:
   (a) Sb by putting a drop of the solution on tin foil (Sec. 77, 4, *a*)
   (b) Sn by the tests with RbCl (p. 400, 3) or $HgCl_2$. In the latter case first reduce tin (IV) to tin (II) by metallic iron

3. Removal of HNO_3 and separation of Pb^{++}. Evaporate the solution in a porcelain basin with a few millilitres of 2 *N* H_2SO_4 until SO_3 fumes appear. Cool, add water, and filter

Precipitate: $PbSO_4$	*Filtrate*: Cu^{++}, Cd^{++}, Al^{+++}, Fe^{+++}, Mn^{++}, Ni^{++}, Zn^{++} (H_2SO_4)

Dissolve on heating in 30% CH_3COONH_4 solution; confirm Pb^{++} in the solution (by test with K_2CrO_4 or KI)

4. Separation of Cu^{++} and Cd^{++}. Precipitate Cu^{++} and Cd^{++} by H_2S in the usual way. Check for complete precipitation, filter and wash the precipitate

Precipitate: CuS, CdS	*Solution*: Al^{+++}, Fe^{++}, Mn^{++}, Ni^{++}, Zn^{++} (H_2S)

5. Test for Cu^{++} and Cd^{++} as in Table 23 (13), starting with the action of 1 *N* HCl. Dissolve CuS precipitate in HNO_3 and test for Cu^{++}	6. Test for Group III cations by Table 18 after evaporation to remove H_2S and heating with 1-2 ml of HNO_3 (sp. gr. 1.2) to oxidize Fe^{++}

Analysis of Aluminium and Its Alloys

1. Dissolving. Treat about 0.5 g of the alloy with a few millilitres of concentrated (25%) caustic alkali solution and 1-2 ml of Na_2CO_3 solution (in case Ca is present), first in the cold and finally on heating. Dilute with water when hydrogen evolution has stopped completely. Filter and wash the precipitate

Precipitate: Cu, Fe, Mn, Ni, Mg, $CaCO_3$

Filtrate: AlO_2^-, ZnO_2^{--}, SnO_2^{--} (NaOH)

2. Tests for Cu^{++}, Fe^{+++}, Mn^{++} and Ni^{++}, and separation from Mg^{++} and Ca^{++}. Dissolve the precipitate * on heating in HNO_3 (sp. gr. 1.2). Test separate portions of the solution for Cu^{++}, Fe^{+++}, Mn^{++} and Ni^{++} by the appropriate reactions. ** Precipitate these ions from the rest of the solution by $(NH_4)_2S$ in the presence of NH_4OH and NH_4Cl as described in Table 18 (3). Filter off the precipitated sulphides

4. Separation of Sn^{++}. Acidify the alkaline solution with HCl and pass H_2S. Filter and wash the precipitate

Precipitate: CuS, Fe_2S_3, MnS, NiS

Filtrate: Ca^{++}, Mg^{++} $[(NH_4)_2S]$

Precipitate: SnS

Filtrate: Al^{+++}, Zn^{++} (HCl, H_2S)

Not investigated

3. Detection of Ca^{++} and Mg^{++}. Acidify with CH_3COOH, evaporate to a small volume, filter off precipitated sulphur, and test the solution for Ca^{++} and Mg^{++} in the usual way (see Table 12)

5. Detection of Sn^{++}. Dissolve the precipitate in concentrated HCl on heating, and test for Sn^{++} by the appropriate reactions

6. Detection of Al^{+++} and Zn^{++}. Boil out H_2S and test for:
   (a) Al^{+++} by the action of NH_4OH in the presence of NH_4Cl or by the spot test with alizarin;
   (b) Zn^{++} by the action of H_2S in the presence of CH_3COONa or by the test with $(NH_4)_2[Hg(CNS)_4]$ in the presence of 0.02% $CoCl_2$ (Sec. 57, 9)

* Instead of the fractional procedure described here, the solution may be analyzed by the usual scheme for mixtures of cations of Groups IV-I (see Table 23) after removal of HNO_3 by evaporation.

** Cu^{++} can be detected by the action of excess NH_4OH (conc.), filtering off the precipitate if necessary. The filtrate can be tested for Ni^{++} after neutralization of excess ammonia by 2 *N* acetic acid.

Table 39

Analysis of Lead, Tin, and Their Alloys

1. Dissolving. Treat about 0.5 g of the alloy with HNO_3 (sp. gr. 1.2) on heating. After some time dilute with an equal volume of water, add a little NH_4NO_3, and continue heating until the alloy is completely decomposed. Filter off the precipitate and wash with hot water containing NH_4Cl

Precipitate: H_2SnO_3 and $HSbO_3$	*Solution*: Pb^{++}, Cu^{++}, Cd^{++}, Fe^{+++}, Zn^{++} (HNO_3)
2. Investigate for Sn and Sb as indicated in Table 37 (2)	3. Separation of Pb^{++}. Add 2 *N* H_2SO_4. Filter and wash the precipitate

Precipitate: $PbSO_4$	*Filtrate*: Cu^{++}, Cd^{++}, Fe^{+++}, Zn^{++}, (Pb^{++})* (HNO_3, H_2SO_4)
4. Dissolve the precipitate on heating in 30% CH_3COONH_4 solution and confirm Pb^{++} by tests with K_2CrO_4 or KI	5. Removal of HNO_3 and detection of individual cations. Evaporate the solution in a porcelain basin until white fumes of SO_3 appear. When cool, add water and filter off additionally precipitated $PbSO_4$. Analyze the solution as described for copper alloys (Table 37, 4-6)

* Remember that precipitation of Pb^{++} by sulphuric acid in the presence of HNO_3 cannot be complete owing to the appreciable solubility of $PbSO_4$ in HNO_3.

If no definite conclusion can be drawn from all the characteristics in Tables 34 and 35 concerning the type of alloy (which may be the case with metals or alloys which do not fit this general classification), find a suitable solvent in accordance with the general rules given in Sec. 112, dissolve about 0.5 g of the alloy in it, and analyze the solution for cations in the usual way.*

If the type of alloy has been established, the alloy is dissolved and analyzed in accordance with one of the tables below (36-39).

Alternatively, alloys may be analyzed by the fractional method with the aid of the spot tests given in Chapter X.

QUESTIONS AND PROBLEMS

1. Why are substances powdered for analysis?
2. Explain why too much substance should not be taken for analysis.
3. How can you confirm that a substance is partially soluble in water?
4. If a substance is partially soluble in water, explain why the solution and the insoluble residue should be analyzed separately.
5. Explain why excess of the acid used to dissolve a substance must be removed by evaporation before analysis.
6. State the advantages and disadvantages of using hydrochloric and nitric acid for dissolving substances.
7. Give examples of substances: (a) insoluble in hydrochloric acid but soluble in nitric; (b) insoluble in nitric acid but soluble in hydrochloric.
8. List the most important substances which are insoluble in acids.
9. State how the following substances may be dissolved: $PbSO_4$, AgCl, AgBr and AgI, $BaSO_4$ and $SrSO_4$.
10. How can the following be brought into solution: native aluminium oxide or the oxide formed by calcination of $Al(OH)_3$; chromic oxide and chromite?
11. By what methods are silicates dissolved?
12. How may SnO_2 and $HSbO_3$ be dissolved?
13. Explain why PO_4^{---} ions must be removed in analysis of cation Groups III, II and I. Describe how this is done.
14. Why is it necessary to neutralize the solution before separation of PO_4^{---} in the form of ferric phosphate, and to remove excess Fe^{+++} ions used for the precipitation? How is this removal effected?
15. Apart from $FePO_4$, what is present in the precipitate formed in separation of phosphate? How is this precipitate analyzed?
16. Why is it preferable to test for anions after analysis for cations?
17. Explain why heavy-metal cations must be removed from the portion of solution to be used for detection of anions. How is this removal effected?
18. Write the equations for the reactions taking place in the formation of the "prepared solution" in analysis of a mixture containing KI, $CaSO_4$, $MgCl_2$ and $Al(NO_3)_3$.
19. Explain why excess acid must not be added during neutralization of the "prepared solution".
20. Which anions may not pass into the "prepared solution", and how can these anions be detected?

---

* The detection of non-metals in alloys is not considered in this book.

CHAPTER X

BRIEF INFORMATION ON SPOT TESTS

116. General Characteristics of the Spot Test Method

We have repeatedly met spot tests for individual cations and anions. However, in systematic analysis they are used for detection of particular ions after separation from interfering ions.

In this chapter we deal with spot tests for separate (fractional) detection of ions. Only the detection of cations in analytical Groups III-V is considered here.

The spot test method of analysis (drop analysis) is one of the most recent methods of qualitative chemical analysis. Its originator was the eminent analyst N. A. Tananaev who, starting in 1920, devised a large number of spot tests, was the first to formulate the principle of fractional analysis by the spot test method, and published the first manual on the subject in which he generalized his work in the form of an original system of spot test analysis. Subsequently A. S. Komarovsky, N. S. Poluektov, and other chemists took part in the development of spot tests in addition to Tananaev and his pupils. The work of the Austrian scientist F. Feigl is of great importance.

Drops of solutions of the reacting substances are used in spot tests. The tests are generally performed on filter paper; a characteristic spot is formed on the paper, the colour of which indicates the presence or absence of a particular ion.

If no suitable colour test for a given ion is available, reactions of other types are used. In such cases, however, the tests are usually performed not on paper but on a spot plate (see Fig. 14, p. 102), on a watch glass, in a crucible or porcelain basin, etc. The use of filter paper for the tests has a number of advantages. On the one hand, the sensitivity of the tests is raised appreciably, and on the other, it may be possible to detect a given ion in the presence of interfering ions without special separation.

For example, if the test for Ni^{++} with dimethylglyoxime is carried out on filter paper, its sensitivity is nearly five times as high (dilution limit 1 : 3,300,000) as in the test on a spot plate or in a test tube (dilution limit 1 : 700,000).

The reason is that filter paper, being full of an enormous number of very fine capillaries (through which the solutions spread), has

a very extensive surface and therefore has a high adsorptive power for dissolved substances. This is easy to demonstrate by the following simple experiment. Put a drop of a dilute solution of any organic dye (such as ink) on a piece of filter paper and let it soak in. All the dye is found to remain in the middle of the moist spot, surrounded by a colourless zone of water. Because of such adsorption of dissolved substances by the paper the actual concentrations during their reactions are considerably higher than in the absence of the paper. It is therefore not surprising that spot tests are more sensitive when performed on filter paper.

The advantages of the spot test method become even more evident if separation is needed for detection of a particular ion. Suppose, for example, that a solution to be tested for Ni^{++} also contains Cu^{++} and Fe^{+++} ions. The first of these gives a pinkish brown colour with dimethylglyoxime and deep blue with ammonia, while the second gives a brown colour with ammonia. These colours may mask the colour formed by the Ni^{++} ion. Therefore Cu^{++} and Fe^{+++} must be separated in the test for Ni^{++}. In spot test analysis this separation can be performed simultaneously with the test itself. A drop of Na_2HPO_4 solution is put on a strip of filter paper; this, the first reagent applied to the paper, is described as the *substrate*. A drop of the unknown solution is then put into the centre of the moist spot. Spreading through the capillaries of the paper, it meets the Na_2HPO_4 present, and as a result the cations giving sparingly soluble phosphates should be precipitated. This precipitation occurs in a definite sequence, dependent on the solubilities of the respective phosphates. *The first to be precipitated, nearest to the centre of the spot, will be the least soluble of the phosphates*, followed by the one of next lowest solubility, etc. The $Ni_3(PO_4)_2$ phosphate, being the most soluble, is precipitated last and is therefore at the periphery of the spot.

In this way Ni^{++} is separated from the cations Fe^{+++} and Cu^{++}, which interfere with its detection. Therefore, if we now treat the spot with ammonia and dimethylglyoxime, we can detect Ni^{++} reliably by the formation of a characteristic red or pink ring around the spot even if these other cations were present in the original solution.

It can be seen that Ni^{++} is separated from the interfering cations owing to the filtering action of the paper, no additional operations being required.

The same is true in most similar cases. In macro-analysis, on the other hand, separation reactions involve much time and work.

As it is possible to separate interfering ions simultaneously with the actual tests, most ions are detected by the *fractional method* in spot test analysis. It is only in relatively rare cases that systematic group analysis has to be used; and even then, because small amounts of

substances are used, the procedure still takes considerably less time than macro-analysis. All this greatly speeds up analysis (according to N. A. Tananaev, the spot test method is from three to ten times as rapid).

Thus, *less time and reagents are required*; *the reactions are specific and often more sensitive*; *very small amounts of the substances are needed for analysis*; these are all very valuable advantages of the spot test method, which ensure its ever-increasing use in factory and research laboratory practice.

Another advantage of the spot test method is that the analyses are carried out without the use of hydrogen sulphide and do not require complicated laboratory equipment. All the apparatus for spot test analysis is extremely simple—small (5-10 ml) reagent bottles, capillary tubes, glass rods with drawn-out tips, and a spot plate (a watch glass, crucible, or even a piece of a broken flask or porcelain basin can be used instead).

Because of the very small volume of this equipment, the spot test method can be widely used on expeditions, which is important in investigations of natural resources.

The ion classification in spot test analysis differs from the classification described in this book for test-tube analysis. For example, N. A. Tananaev subdivides all cations into the following two groups.

Group I. Potassium, sodium, ammonium, magnesium, calcium, strontium, barium, arsenic, antimony, and tin, not precipitated by excess $(NH_4)_2S$.

Group II. Aluminium, chromium, iron, manganese, zinc, cobalt, nickel, silver, lead, mercury, copper, bismuth, and cadmium, precipitated by $(NH_4)_2S$.

Spot tests for all the cations cannot be described in this brief manual. Similarly, we will not discuss tests for anions, but will deal only with detection of cations of Group II (in Tananaev's classification)* and of arsenic, antimony, and tin, as spot tests for these ions are the most important and interesting. Those wishing to learn about spot tests in greater detail should consult the specialized manuals.

117. Spot Tests for Individual Cations

It must be remembered when carrying out spot tests that the order in which the reagents are put on the paper is often of very great importance and should not be varied arbitrarily. If this rule is not obeyed, many tests become less sensitive or even fail completely.

---

* Tananaev's classification of cations into groups is adopted throughout this chapter.

All the instructions with regard to operating techniques must also be followed exactly, because only then are the results sufficiently clear and definite. The techniques should preferably be demonstrated by the instructor. This will ensure the avoidance of errors which beginners make almost inevitably.

The tests given below are intended in most cases for detection of each ion in the presence of all the other Group II cations.

However, a test carried out with a solution containing only the ion sought usually gives somewhat different results from the same test in the presence of various extraneous ions. The following procedure for studying the tests is therefore advisable.

(a) The test is first carried out with a pure salt of the given cation.

(b) It is repeated with a mixture of the nitrates of all the cations of the group (apart from salts of Fe^{++} and Hg_2^{++})*.

(c) Finally, the test is carried out with a mixture of the same salts but without a salt of the cation sought.

In some cases, for example, if it is known that a test is masked by a particular cation, this scheme should be suitably modified.

Before describing the actual tests, let us examine *the technique of putting the drops on the paper.*

Glass tubes with one end drawn out to a fine capillary are used for this purpose in spot analysis. The capillary is immersed into the solution to a depth of 1-2 mm, and the solution rises in the tube to a certain height which depends on the capillary diameter. The capillary tip is then brought into contact with a strip of filter paper about 1 cm wide and left until a moist spot 2-3 mm in diameter has formed on the paper; the capillary is then quickly removed.

Excessively large drops, which are not completely absorbed, *should never be put on the paper*, because then the liquid flows down in a stream to one side without reacting with the solution previously put on the paper. As a result, the test becomes indistinct. To avoid this, never take more liquid into the capillary than can be held there by capillary forces. *The liquid must never drip from the capillary on to the paper* but must be slowly absorbed by the paper in contact with the capillary tip.

All the reagent bottles used in spot test analysis must be fitted with pipettes with their ends drawn out to fine capillaries. The reagent bottles are kept in a special box.

To avoid contamination of the reagents, the tip of the capillary must be brought into contact with a clean paper surface before the pipette is inserted into the bottle. This removes the drop of contami-

* In spot analysis these cations are usually oxidized by nitric acid to Fe^{+++} and Hg^{++}, and we will not study their reactions. It is not always possible to use chlorides or sulphates instead of nitrates, because when the mixture is prepared certain cations (for example, Ag^{+} and Pb^{++}) may be precipitated.

nated reagent from the pipette. If this rule is not obeyed, the reagents soon become unusable.

Soft and relatively thick paper should be used for spot tests. If such paper is not available, ordinary filter paper folded in half may be used.

1. Test for Fe^{+++}. The most usual spot test for Fe^{+++} depends on the reaction with KI and $K_3[Fe(CN)_6]$, carried out as follows.

(a) Put a drop of $K_3[Fe(CN)_6]$ solution (substrate) on a drop of filter paper.

(b) Put a drop of the unknown solution in the centre of the moist spot.

(c) Add a drop of KI solution. The following reactions take place:

$$2FeCl_3 + 2KI = 2FeCl_2 + 2KCl + \downarrow I_2$$

$$3FeCl_2 + 2K_3[Fe(CN)_6] = \downarrow Fe_3[Fe(CN)_6]_2 + 6KCl$$

The salt formed, $Fe_3[Fe(CN)_6]_2$, has a characteristic blue colour (Turnbull's blue). However, this colour is masked by the free iodine liberated, which colours the whole spot brown.

(d) Draw the tip of a capillary containing $Na_2S_2O_3$ right across the spot. The brown colour of iodine disappears as the result of the reaction

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

and the blue colour due to Turnbull's blue appears clearly. This colour is the sign that Fe^{+++} is present.

Before testing for Fe^{+++}, confirm that the paper is free from iron compounds. The simplest way to do this is to put on in a drop of NH_4CNS followed by a drop of HCl. If a red-brown colour is formed [due to $Fe(CNS)_3$], the paper is unsuitable.*

2. Test for Al^{+++}. The alizarin test (Sec. 53, 6) is used as a spot test for Al^{+++}. We have already seen that this test gives a red compound of Al^{+++} with alizarin, known as aluminium lake. Many other cations form similar coloured lakes. They must therefore be separated from Al^{+++}. This is achieved by the use of $K_4[Fe(CN)_6]$ as a substrate. Interfering cations form sparingly soluble ferrocyanides with $K_4[Fe(CN)_6]$ and therefore remain in the centre of the spot. Al^{+++} ions, not precipitated by $K_4[Fe(CN)_6]$, diffuse to the edges of the spot, where they can be detected by the action of alizarin in the presence of NH_4OH.

The test is carried out by the following technique.

(a) Put a drop of $K_4[Fe(CN)_6]$ solution on a strip of filter paper.

---

* This test can also be used as a test for Fe^{+++} in the unknown solution. However, it is less reliable than the test with KI and $K_3[Fe(CN)_6]$, as a number of substances can interfere.

(b) Put a drop of the unknown solution in the centre of the spot.

(c) Treat the spot with ammonia gas by holding the paper over the mouth of a bottle with concentrated ammonia until the paper smells distinctly of ammonia.

(d) Moisten the outer rim of the spot with alizarin solution.

(e) Again treat the spot with ammonia gas.

A pink ring on a violet background appears in the presence of Al^{+++}. Only the pink ring is a sign of the presence of Al^{+++}; the violet background is due to the presence of NH_4OH and alizarin and is not significant. When the spot dries, the NH_4OH volatilizes and the pink colour becomes more distinct.

In the presence of a high concentration of Cu^{++} ions the above procedure becomes unreliable and should be modified as follows.

(a) Put a drop of $K_4[Fe(CN)_6]$ solution on filter paper.

(b) Put the unknown solution in the centre of the spot.

(c) Add Na_2S solution.

(d) Add HCl solution.

The action of Na_2S converts Cu^{++} and Al^{+++} into CuS and $Al(OH)_3$. The first of these is insoluble in HCl and therefore remains in the centre of the spot when HCl is added. On the other hand, $Al(OH)_3$ is soluble in HCl and as a result Al^{+++} ions diffuse to the edge of the spot, where they can be detected by the action of NH_3, followed by alizarin solution and NH_3 again (see the method described above).

Tin and antimony also interfere in the test for Al^{+++}. If these ions are present (see below, 14 and 15), proceed as follows. First, oxidize Sn^{++} to Sn^{++++} by sodium peroxide by adding NaOH to a few drops of the solution on a watch glass until strongly alkaline, followed by Na_2O_2. Pour the slightly turbid liquid on to another watch glass and add excess concentrated acetic acid. This precipitates $Sn(OH)_4$ and $Sb(OH)_3$ while Al^{+++} remains in solution and can be detected as described above.

Experience is needed to be able to distinguish the colours in these tests for Al^{+++}. To gain this experience, carry out the spot test with solutions containing various combinations of cations, with and without Al^{+++}.

3. Test for Cr^{+++}. To test for Cr^{+++}, it is first oxidized to CrO_4^{--} by the action of Na_2O_2:

$$2Cr^{+++} + 3Na_2O_2 + 4OH^- = 2CrO_4^{--} + 6Na^+ + 2H_2O$$

The other Group II cations are precipitated as the hydroxides, such as $Fe(OH)_3$, $Co(OH)_3$, $MnO(OH)_2$, etc. The equations are:

$$2Co^{++} + Na_2O_2 + 2OH^- + 2H_2O = \downarrow 2Co(OH)_3 + 2Na^+$$

$$Mn^{++} + Na_2O_2 + H_2O = \downarrow MnO(OH)_2 + 2Na^+$$

The benzidine test is used to detect the CrO_4^{--} ions formed (see p. 273).

The test is carried out as follows.

(a) Put a few drops of the unknown solution on a watch glass, add excess of solid Na_2O_2, and warm slightly. Dilute with 2-3 drops of water.

(b) Transfer a drop of the liquid together with the precipitate to paper by touching the paper with the capillary tip and holding it there until a fairly wide (1-2 mm) aqueous spot (containing the CrO_4^{--} ion) is formed around the precipitate which remains in the centre.

(c) Draw the tip of a capillary containing benzidine solution around the spot. A characteristic blue colour around the spot is a sign of the presence of Cr^{+++} in the unknown solution.

It must be remembered when carrying out this test that benzidine can be oxidized not only by CrO_4^{--} ions but also by other oxidizing agents, such as $MnO(OH)_2$ and $Co(OH)_3$, formed by the action of Na_2O_2 on the cations Mn^{++} and Co^{++}.

However, being insoluble, $MnO(OH)_2$ and $Co(OH)_3$ remain in the middle of the spot while CrO_4^{--} ions diffuse to the edge. Therefore care must be taken in the test that benzidine does not penetrate to the centre of the spot, as otherwise a blue colour may appear even in the absence of chromium owing to oxidation of benzidine by $MnO(OH)_2$ or $Co(OH)_3$. *Therefore the test for chromium is conclusive only if there is a zone not coloured blue between the precipitate and the blue region of the spot.*

4. Test for Mn^{++}. The most usual spot test for Mn^{++} is based on its ability to reduce Ag^+ to metallic silver in alkaline solution:

$$Mn(NO_3)_2 + 2AgNO_3 + 4NH_4OH = \downarrow 2Ag + \downarrow MnO(OH)_2 + 4NH_4NO_3 + H_2O$$

The procedure is as follows.

(a) Put a drop of the unknown solution on a strip of filter paper.

(b) Add a drop of ammoniacal $AgNO_3$ solution (reagent for Mn^{++});* warm slightly.

In the presence of manganese the spot turns black owing to formation of metallic silver.

Unless the heating is carried out cautiously, Ag^+ may be reduced by the paper, giving a black colour in the absence of manganese; therefore a "blank" test should be carried out to prevent error. For this purpose a drop of the reagent without the unknown solution is put by the side of the spot used for the test and the paper is warmed so that the blank spot does not turn black.

* To prepare this reagent, add concentrated NH_4OH to saturated $AgNO_3$ solution until the precipitate initially formed dissolves. Then add as much NH_4OH solution as has already been added.

Another test for Mn^{++} is based on the ability of $MnO(OH)_2$ to oxidize benzidine (p. 283).

Proceed as follows.

(a) Put a drop of the unknown solution on filter paper.

(b) Treat the spot with gaseous ammonia. $Mn(OH)_2$ is formed, which is rapidly oxidized by atmospheric oxygen to $MnO(OH)_2$ and the spot turns brown.

(c) Moisten the spot with benzidine. A blue colour indicates the presence of Mn^{++}.

If Co^{++} is present, a faint blue colour may be formed owing to formation of $Co(OH)_3$, which can also oxidize benzidine. However, this can be avoided if a drop of NH_4Cl, which forms a complex salt with cobalt, is added before the ammonia treatment.

This test is unreliable in the presence of Ag^+.

5. Test for Ni^{++}. The Ni^{++} ion is detected by means of dimethylglyoxime in the presence of NH_4OH on a substrate of Na_2HPO_4, which precipitates interfering cations in the centre of the spot. The test procedure is as follows.

(a) Put a drop of Na_2HPO_4 solution on filter paper.

(b) Put a drop of the unknown solution in the middle of the spot.

(c) Add a drop of Na_2HPO_4 solution.

(d) Add a drop of dimethylglyoxime.

(e) Treat the spot with ammonia gas.

In the presence of Ni^{++} a pink ring is formed; at a high Ni^{++} concentration the whole spot may become pink.

The Fe^{++} ion also gives a red colour with dimethylglyoxime, masking the test for nickel. Therefore ferrous iron must first be oxidized to Fe^{+++}.

6. Test for Co^{++}. The Co^{++} ion is detected as a complex thiocyanate, formed by the reaction

$$Co(NO_3)_2 + 4KCNS = K_2[Co(CNS)_4] + 2KNO_3$$

which is blue in the anhydrous state.

The test is carried out as follows.

(a) Put a drop of KCNS (or NH_4CNS) solution on a strip of filter paper.

(b) Add a drop of the unknown solution.

(c) Add another drop of KCNS.

(d) Treat the coloured spot with ammonia gas and dry cautiously over a burner flame.

In the presence of Co^{+++} a blue ring appears as the paper dries; it is best seen if the paper is held up to the light.

A brown colour may appear with incautious heating, owing to charring of the paper and decomposition of the thiocyanate.

7. Test for Ag^+. The silver ion is precipitated as AgCl; the precipitate is washed thoroughly with water (to remove all interfering cations) and then treated with $Mn(NO_3)_2$ and NaOH solutions. A reaction similar to that used in the test for Mn^{++} occurs:

$$2AgCl + Mn(NO_3)_2 + 4NaOH = \downarrow 2Ag + 2NaCl + 2NaNO_3 + \downarrow MnO(OH)_2 + H_2O$$

The metallic silver colours the central part of the spot black.

The test is performed in the following sequence.

(a) Put a drop of HCl solution on the paper.

(b) Put a drop of the unknown solution in the centre of the spot.

(c) Wash the precipitate formed with water as follows. Take up as much water as can be held by capillary forces in a thin capillary tube with even edges, press it down firmly in the middle of the spot, and hold it there until the spot grows to 2-3 times of its original diameter. If necessary, the capillary may be refilled with water and the operation repeated, etc. As the result of this treatment, AgCl (possibly $PbCl_2$) remains in the centre of the spot, followed by a zone of pure water surrounded by a zone of impurities washed out of the precipitate.

(d) Moisten the thoroughly washed precipitate with a drop of $Mn(NO_3)_2$ solution.

(e) Put a small drop of concentrated NaOH in the centre of the spot. In the presence of Ag^+ the central part of the spot immediately turns black. Slow blackening is the consequence of oxidation of $Mn(OH)_2$ to $MnO(OH)_2$. To avoid error it is helpful to carry out a "blank" test with a drop of $Mn(NO_3)_2$ moistened with a drop of NaOH by the side of the test spot.

8. Test for Pb^{++}. The Pb^{++} ion can be detected by the formation of a black precipitate of PbS with Na_2S. As sodium sulphide gives black precipitates with several other cations (e. g., Fe^{+++}, Co^{++}, Ni^{++}, Cu^{++}, Ag^+), the test is conducted as follows.

(a) Put a drop of H_2SO_4 solution on a strip of filter paper.

(b) Put a drop of the unknown solution in the centre of the spot.

(c) Add another drop of H_2SO_4 solution.

(d) Wash the $PbSO_4$ precipitate thoroughly, as described in the test for Ag^+.

(e) Draw a capillary containing Na_2S solution across the whole spot.

Blackening of the central part of the spot indicates the presence of Pb^{++}. Blackening may also occur in regions containing the washed-out Cu^{++}, Ag^+ and other cations, at the edges of the spot.

If the washing is performed correctly, there should be the colourless zone between the black periphery and the centre.

The presence of a colourless zone indicates that all the interfering cations have been displaced to the periphery. Obviously, in the absence of a colourless zone the test cannot be relied upon; it must be carried out again with more careful washing of the precipitate.

In the absence of Pb^{++} blackening can occur only at the edges and not in the middle of the spot.

This test is unreliable in the presence of large amounts of Ag^{+}, because H_2SO_4 may cause the precipitation of Ag_2SO_4, which is also blackened by Na_2S. In such cases the washed precipitate may be treated with a drop of a special reagent [consisting of KI, $SnCl_2$ and $Cd(NO_3)_2$] instead of Na_2S. This reagent gives a characteristic orange-red colour, due to formation of the complex $Pb_2[SnI_6]$, in the presence of lead.

Ag^{+} and other Group II cations do not interfere with this test. If the solution contains Bi^{+++} in addition to Pb^{++}, a brown colour is obtained. This is an indication of the presence of both cations.

It will be remembered that Pb^{++} can also be detected by the spot test with benzidine, described on p. 353. However, this test cannot be used in the presence of Mn^{++}, because the $MnO(OH)_2$ precipitated under the test conditions can also oxidize benzidine.

9. Test for Hg^{++}. In alkaline solution the Ag^{+} ion is reduced by $SnCl_2$ to metallic silver. In acid solution this reduction occurs only in the presence of Hg^{++} in the solution. This is the basis of the following test for Hg^{++}.

(a) Put a drop of $SnCl_2$ solution containing free HCl on a strip of filter paper.

(b) Put a drop of $AgNO_3$ solution in the middle of the spot*.

(c) Add a drop of the unknown solution.

Intensive blackening of the spot (liberation of silver) indicates the presence of Hg^{++}. To intensify the effect, the spot may be remoistened with a drop of $AgNO_3$.

In the absence of Hg^{++} the spot may turn grey-violet after some time owing to decomposition of AgCl by the action of light.

The following characteristic reaction also often works.

(a) Put a drop of KI solution on a strip of filter paper.

(b) Put the unknown solution in the centre of the spot, keeping the capillary tip in contact with the paper for several seconds.

In the presence of Hg^{++} a reddish-orange spot or ring due to HgI_2 is formed. This is often surrounded by a wider steel-grey ring of BiI_3 and a brown ring due to iodine. The iodine is formed by the action of copper or ferric salts on KI.

---

* If the spot turns black on addition of $AgNO_3$ before the unknown solution has been added, this indicates that the $SnCl_2$ solution did not contain sufficient hydrochloric acid.

To remove the colour due to iodine, the spot should be moistened with Na_3AsO_3 solution containing $NaHCO_3$. The orange HgI_2 ring is then more distinct.

10. Test for Cu^{++}. Cupric cyanide, $Cu(CN)_2$ is extremely unstable and is reduced to CuCN as soon as it is formed (see footnote on p. 358). It therefore oxidizes benzidine to form a blue product. This is the basis of the following test for Cu^{++}.

(a) Put a drop of the unknown solution on a strip of filter paper.

(b) Add a drop of benzidine solution.

(c) Finally, add a drop of KCN solution (*Poison!*)*.

The spot turns blue in the presence of Cu^{++}.

This test is unreliable in the presence of Ag^+ or Fe^{++}.

Another spot test for Cu^{++} is based on the reaction of copper salts with KI solution:

$$2Cu(NO_3)_2 + 4KI = \downarrow 2CuI + I_2 + 4KNO_3$$

If the liberated iodine is decolourized by Na_3AsO_3 solution, a white precipitate of CuI remains. This is a powerful reducing agent, capable of reducing Ag^+ ions to metallic silver:

$$Cu^+ + Ag^+ = Cu^{++} + \downarrow Ag$$

Proceed as follows.

(a) Put a drop of a solution of AgI in KI on a strip of filter paper**.

(b) Hold a capillary with the unknown solution in the centre of the spot for several seconds.

(c) Again touch the spot with a capillary containing a solution of AgI in KI.

(d) Wash the centre of the spot with water (see p. 523, 7).

(e) Moisten the spot with a drop of Na_3AsO_3 solution; the brown colour due to iodine disappears.

(f) Touch the centre of the spot with the capillary tip containing saturated $AgNO_3$ solution.

Blackening of the spot, due to liberation of metallic silver, indicates the presence of Cu^{++} in the unknown solution. In the absence of copper, a pale yellow spot of AgI is formed.

Finally, a spot test*** based on the reaction of Cu^{++} with ammonia and $K_4[Fe(CN)_6]$ may be recommended.

(a) Put a drop of concentrated NH_4OH solution on a strip of filter paper.

---

* Saturated KBr solution may be used instead of KCN, because $CuBr_2$ is also easily reduced to CuBr, oxidizing benzidine. The spot should be warmed slightly if KBr is used.

** To prepare this solution, put a drop of $AgNO_3$ solution on a watch glass and add concentrated KI drop by drop until the initially precipitated AgI has redissolved.

*** Technique devised by L. M. Orlova.

(b) Put a drop of the unknown solution followed by another drop of ammonia in the centre of the spot. Ammonia precipitates a number of cations in the form of hydroxides, which remain in the centre of the spot, while Cu^{++} diffuses to the periphery in the form of $[Cu(NH_3)_4]^{++}$ complex ions.

(c) Dry the moist spot (to remove ammonia and to decompose the complex with the copper ion) and ring it round with a capillary containing $K_4[Fe(CN)_6]$ solution. The formation of a brown ring of $Cu_2[Fe(CN)_6]$ indicates the presence of copper.

11. Test for Bi^{+++}. In distinction from the other tests, the spot test described below is conducted in a small porcelain basin and not on paper. Put a drop of the unknown solution in the basin and add excess KI. Free iodine may be formed by oxidation of KI by Cu^{++} or Fe^{+++} ions. To remove it, evaporate the solution to dryness, moisten the dry residue with a drop of KI solution, dilute with 2-3 drops of water and heat to boiling.

In the presence of Bi^{+++} a water-soluble complex salt, $K[BiI_4]$, is formed. This confers a characteristic orange or yellow colour, which does not disappear on heating, to the solution.

In the presence of Pb^{++} a yellow precipitate of PbI_2 is formed. In such cases the colour of the solution is detected as follows. Tilt the basin *cautiously and slightly*; the solution flows down the wall of the basin free from precipitate and its colour can be easily seen.

12. Tests for Cd^{++} and Zn^{++} by N. A. Tananaev's method involve systematic analysis, and are performed as follows.

Treat six drops of the unknown solution (which may contain all the cations of the analytical Groups III and IV) on a watch glass with a large excess of ammonia (until a sharp odour appears) and warm slightly. Some of the cations are precipitated as hydroxides while some, namely Ag^+, Cu^{++}, Co^{++}, Ni^{++}, Zn^{++} and Cd^{++}, remain in solution as ammine complexes.

The precipitate is separated from the solution by filtration.

The filtration technique in spot test analysis is usually as follows. Fold a strip of paper 2-3 mm wide and about 1 cm long into four, moisten it with a drop of water, and put on a watch glass near the liquid with the precipitate. Place a capillary with even edges on this strip at right angles, without excessive pressure, and move the strip into the liquid. Then suck the liquid (by the mouth) into the capillary. Before entering the capillary the liquid passes through the paper layers which retain the precipitate completely.

Put the filtrate in a porcelain basin, evaporate to dryness, and heat the residue strongly to decompose ammonium salts completely. Dissolve the residue in a few drops of HCl, remove excess acid by *cautious* evaporation to dryness, and dissolve the chlorides in a few drops of water. If Ag^+ was present in the unknown solution, white

turbidity due to AgCl remains; in that case the liquid is filtered as described above.

Treat the solution with excess Na_2O_2 (until distinctly alkaline), stir, heat to boiling, and dilute with about 5 ml of hot water. After 3-5 minutes of settling filter off the precipitate.

The reaction of Na_2O_2 with water yields NaOH, which precipitates the hydroxides of copper, cobalt, nickel and cadmium. Zinc remains in solution as zincate, and may be detected by the usual tests, as described below.

(a) Treat a portion of the filtrate with a few drops of Na_2S or $(NH_4)_2S$ solution; in the presence of zinc a white turbidity due to ZnS appears, insoluble in CH_3COOH but dissolved by HCl.

(b) Acidify another portion of the filtrate with acetic acid and add $K_4[Fe(CN)_6]$ solution; a white precipitate of $K_2Zn_3[Fe(CN)_6]_2$ is formed.

To test for Cd^{++}, wash the precipitate obtained during separation of Zn^{++} by the action of Na_2O_2 with hot water (after filtration is complete), decanting the water cautiously from the precipitate; then dissolve it on warming in a few drops of acetic acid, filter if necessary, and neutralize with ammonia. The ammine complexes of the various cations are formed. KCN solution is added (drop by drop until the colour disappears) to convert the ammines into cyanide complexes.

Now add Na_2S or $(NH_4)_2S$ solution to the liquid; only the least stable of the complexes, $[Cd(CN)_4]^{--}$, gives a sulphide precipitate. Therefore a yellow turbidity of CdS, which aggregates into grains on stirring, indicates the presence of Cd^{++}.

13. Arsenic ions are detected in spot test analysis either by reduction to AsH_3 in alkaline or acid solution (by Tananaev's method), or by reduction to free As. These reactions, as used for spot tests, were described earlier (see pp. 391 and 392).

The following points must be remembered.

(a) Reduction to metallic arsenic can be used for detection of As compounds, in either the As^{III} or the As^{V} form, in the presence of all other cations.

(b) Reduction to AsH_3 by metallic aluminium (or zinc) in alkaline solution is possible only in the case of As^{III} compounds.

(c) Reduction to AsH_3 by magnesium (or zinc) in acid solution is masked by the presence of antimony.

14. Tests for Tin Ions. Put a drop of the reagent*, consisting of $Hg(NO_3)_2$ and $AgNO_3$, on filter paper, followed by a drop of the unknown solution. A black spot appears in the presence of Sn^{++}

* To prepare the reagent, add 2-3 drops of nitric acid to saturated aqueous $Hg(NO_3)_2$ solution. Add enough solid $AgNO_3$ to give a 20% solution. The reagent is unstable and should be prepared as required.

owing to reduction of Ag^+ to metallic silver. This reaction has already been described in the spot test for Hg^{++} (see above, 9).

Another test for tin is based on the following reaction. Excess $HgCl_2$ reacts with $SnCl_2$ in acid solution as follows:

$$2HgCl_2 + SnCl_2 = \downarrow Hg_2Cl_2 + SnCl_4$$

If $SnCl_2$ is present in large excess by comparison with $HgCl_2$, the latter is reduced to metallic mercury. In alkaline solution reduction to metallic mercury may occur in the presence of very small amounts of Sn^{++} ions. Even such a weak base as aniline, $C_6H_5NH_2$, can produce the alkalinity required for this reaction. This distinguishes Sn^{++} from Sb^{++++} ions; the latter reduce Hg^{++} to metallic mercury in the presence of stronger bases, but not in the presence of aniline.

The test procedure is as follows.

(a) Soak a strip of filter paper in $HgCl_2$ solution and dry it.

(b) Put a drop of the unknown solution (not too acid) on this paper, followed by a drop of aniline. A black spot of metallic mercury appears in the presence of Sn^{++}. This test is highly sensitive, and can be used for detecting Sn^{++} in the presence of any other ions.

These tests are based on the reducing action of Sn^{++} ions. Therefore if tin is present in the form of Sn^{++++} it must first be reduced to Sn^{++} as follows. Add 2-3 drops of hydrochloric acid to a drop of the unknown solution on a watch glass, and put in a small piece of magnesium. The following reaction occurs:

$$Sn^{++++} + Mg = Sn^{++} + Mg^{++}$$

If the solution is not acid enough, the reduction may go as far as the formation of metallic tin, deposited in the form of a grey spongy mass. If this happens, add 2-3 more drops of HCl, when the tin dissolves rapidly. Test the solution as described above.

15. Test for Sb^{+++}. Put 2-3 drops of the unknown (acid) solution on a piece of tin foil and leave for some time. In the presence of antimony ions a black or brown spot of metallic antimony is formed. Several cations, such as Bi^{+++}, Ag^+, Pb^{++}, etc., interfere; being to the right of tin in the potential series, they are also reduced to the free metals.

The Sb^{+++} ion can also be detected by the action of sodium phosphomolybdate solution on a drop of $SbCl_3$ solution on paper; a blue colour appears owing to reduction of Mo^{VI} to compounds of lower valencies.

The Sn^{++} ion gives a similar colour. However, according to Tananaev, this test can be used for detecting antimony in the presence of Sn^{++} (and all other cations) by the following procedure. Put a drop

of concentrated ammonia on a strip of paper, followed by the unknown solution and another drop of ammonia. $Sn(OH)_2$, $Sn(OH)_4$, $Sb(OH)_3$ and other hydroxides are precipitated in the middle of the spot. Press the tip of a capillary filled with concentrated acetic acid, in which $Sn(OH)_2$ dissolves, against the precipitate; Sn^{++} ions diffuse to the periphery. Now touch the precipitate with a capillary containing $HgCl_2$ solution; the Sn^{++} ions still remaining in the centre of the spot are oxidized by Hg^{++} ions to Sn^{++++}. Now draw a capillary with hydrochloric acid across the spot (making sure to include the centre), followed by a capillary with sodium phosphomolybdate solution drawn along the same line. In the presence of Sb^{+++} the centre of the spot turns blue. If Sn^{++} ions were present in the solution, two blue lines also appear at the periphery of the spot. Obviously, a *colourless zone* must remain between these lines and the central spot, indicating complete removal of Sn^{++} ions from the centre.

APPENDICES

I. Reagents used in qualitative analysis

Commercial reagents are sold in the following five purity grades: (1) technical; (2) purified; (3) pure; (4) pure for analysis (A.R.); (5) chemically pure (C.P.). Chemically pure reagents have the lowest impurity contents. Pure and A. R. reagents may be used for most analytical work, but in some cases only C.P. reagents are suitable.

The reagents and solutions used in qualitative analysis are listed below, together with instructions for preparation.

A. Acid Solutions

Name and formula	Density at 20°, g/cm³	Normality (approx.)	Content by weight, %	Preparation
		Inorganic acids		
Hydrochloric, HCl				
concentrated . . .	1.19	12	37.23	
dilute	—	2	7.15	Mix 836 ml of water with 167 ml of HCl (sp. gr. 1.19)
Nitric, HNO_3				
concentrated . . .	1.42	16	69.80	
dilute	1.2	6	32.36	Mix concentrated HNO_3, sp. gr. 1.42, with an equal volume of distilled water
Sulphuric, H_2SO_4				
concentrated . . .	1.84	36	95.60	
dilute	—	2	9.25	Slowly add 55 ml of H_2SO_4, sp. gr. 1.84, to 945 ml of water with continuous stirring

Cont'ed

Name and formula	Density at 20°, g/cm³	Normality (approx.)	Content by weight, %	Preparation
		Organic acids		
Acetic, CH_3COOH				
concentrated . . .	1.05	17	99.5	
dilute	—	2	12.10	Mix 116 ml of concentrated acetic acid with 884 ml of water
Tartaric, $H_2C_4H_4O_6$	—	2	—	Dissolve 150 g of tartaric acid in a small amount of water and dilute to 1 litre

B. Alkali Solutions

Name and formula	Normality (approx.)	Preparation
Ammonia, NH_4OH		
concentrated (25-27% NH_3, sp. gr. 0.9)	13	—
dilute	2	Mix 687 ml of water with 133 ml of concentrated ammonia, sp. gr. 0.9
Baryta water, $Ba(OH)_2$ . .	0.4	Saturated solution [contains 63 g of $Ba(OH)_2 \cdot 8H_2O$ per litre]
Caustic potash, KOH . .	2	Dissolve 112 g KOH in water and dilute to 1 litre
Caustic soda, NaOH		
concentrated	6	Dissolve 250 g NaOH in water and dilute to 1 litre
dilute	2	Dissolve 80 g NaOH in water and dilute to 1 litre
Lime water, $Ca(OH)_2$ . . .	0.05	Saturated solution contains 1.3 g CaO per litre

Cont'ed

Name and formula	Normality (approx.)	Preparation
C. Solutions of Ammonium Salts		
Ammonium acetate, CH_3COONH_4	4	Dissolve 300 g of the commercial salt in water and dilute with water to 1 litre
Ammonium carbonate, $(NH_4)_2CO_3$ (group reagent for cation Group II) . .	2	Dissolve 96 g of the powdered commercial salt in 1 litre of 2 *N* NH_4OH
Ammonium carbonate (reagent for Cl^-)	2.5	Dissolve 140 g of the commercial salt in 860 ml of water
Ammonium chloride, NH_4Cl	1	Dissolve 54 g of the salt in water, dilute to 1 litre
Ditto (saturated solution)	—	Dissolve 290 g of the salt in 1 litre of water and filter
Ammonium fluoride, NH_4F	—	Saturated aqueous solution of the commercial salt
Ammonium molybdate, $(NH_4)_2MoO_4$*	—	Dissolve 50 g of the commercial salt in 500 ml of water with warming, and dilute to 1 litre
Ammonium nitrate, NH_4NO_3	2.5	Dissolve 200 g of the salt in water, dilute to 1 litre
Ammonium oxalate, $(NH_4)_2C_2O_4$	0.5	Dissolve 35 g of the salt in water and dilute to 1 litre
Ammonium persulphate, $(NH_4)_2S_2O_8$	0.5	Dissolve 57 g of the salt in water and dilute to 1 litre
Ammonium sulphate, $(NH_4)_2SO_4$	—	Dissolve 50 g of the salt in 100 ml of hot water. Cool and filter

*Solution used for studying the reactions of MoO_4^{--}. Preparation of the ammonium molybdate solution used as a reagent is given in Appendix I, E.

Cont'ed

Name and formula	Normality (approx.)	Preparation
Ammonium sulphide, $(NH_4)_2S$	6	Pass H_2S through 200 ml of concentrated NH_4OH until no more is absorbed. Add 200 ml more of concentrated NH_4OH and dilute to 1 litre
Ammonium thiocyanate, NH_4CNS	0.5	Dissolve 38 g of the salt in water and dilute to 1 litre
Ammonium thiocyanate, NH_4CNS (for testing for Co^{++})	—	Saturated aqueous solution of the commercial salt

D. Solutions of Other Salts

Name and formula	Molecular weight	Concentration		Notes
		N	g/litre*	
Aluminium chloride, $AlCl_3 \cdot 6H_2O$	241.4	0.5	40.2	
Antimony (III) chloride, $SbCl_3$	228.1	0.5	38.0	Dissolve in HCl (1 : 1)
Barium chloride, $BaCl_2 \cdot 2H_2O$	244.3	0.5	61.1	
Bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$	485.1	0.5	80.6	Dissolve in presence of HNO_3
Cadmium nitrate, $Cd(NO_3)_2 \cdot 4H_2O$	308.5	0.5	77.1	
Calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$	236.2	0.5	59.0	
Calcium sulphate, $CaSO_4 \cdot 2H_2O$	172.2	0.03	2	Saturated solution
Chromium (III) chloride, $CrCl_3 \cdot 6H_2O$	266.5	0.5	44.4	
Cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$	291.1	0.5	72.8	

*The number of grams of salt indicated in this column is dissolved in a small amount of water and diluted to 1 litre.

Cont'ed

Name and formula	Molecular weight	Concentration		Notes
		N	g/litre *	
Copper nitrate, $Cu(NO_3)_2 \cdot 3H_2O$	241.6	0.5	60.4	
Ferric chloride, $FeCl_3 \cdot 6H_2O$	270.3	0.5	45.0	
Lead acetate, $(CH_3COO)_2Pb \cdot 3H_2O$	379.3	0.5	95.0	
Lead nitrate, $Pb(NO_3)_2$	331.2	0.5	82.8	
Magnesium chloride, $MgCl_2 \cdot 6H_2O$	203.3	0.5	50.8	
Manganese nitrate, $Mn(NO_3)_2 \cdot 6H_2O$	287.0	0.5	71.7	
Mercuric chloride, $HgCl_2$	271.5	0.2	27.2	
Mercurous nitrate, $Hg_2(NO_3)_2 \cdot 2H_2O$	561.3	0.2	56.1	
Nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$	290.8	0.5	72.7	
Potassium bromide, KBr	119.0	0.5	59.5	
Potassium chloride, KCl	74.6	0.5	37.3	
Potassium chromate, K_2CrO_4	194.2	0.5	48.5	
Potassium dichromate, $K_2Cr_2O_7$	294.2	1.5	73.8	
Potassium ferricyanide, $K_3[Fe(CN)_6]$	329.2	1	109.7	
Potassium ferrocyanide, $K_4[Fe(CN)_6] \cdot 3H_2O$	422.4	1	105.6	
Potassium iodide, KI	166.0	0.5	83.0	
Potassium nitrate, KNO_3	101.1	0.5	50.5	
Potassium nitrite, KNO_2	85.1	0.5	42.5	
Potassium permanganate, $KMnO_4$	158.0	0.5	15.8	
Silver nitrate, $AgNO_3$	169.9	0.1	17.0	
Sodium acetate, CH_3COONa	136.1	1	136.1	
Sodium arsenite, Na_3AsO_3	191.9	0.5	32.0	
Sodium carbonate, Na_2CO_3	106.0	0.5	26.5	
Ditto	106.0	3.0	159.0	
Sodium chloride, NaCl	58.5	0.5	29.3	
Sodium hydrogen arsenate, $Na_2HAsO_4 \cdot 12H_2O$	402.2	0.5	67.0	
Sodium hydrogen phosphate, $Na_2HPO_4 \cdot 12H_2O$	358.2	0.5	59.7	
Sodium hydrogen tartrate, $NaHC_4H_4O_6$	172.1	1	172.1	

Cont'ed

Name and formula	Molecular weight	Concentration		Notes
		N	g/litre *	
Sodium nitrate, $NaNO_3$ . . .	85.0	0.5	42.5	
Sodium nitrite, $NaNO_2$ . . .	69.0	0.5	34.5	
Sodium sulphate, $Na_2SO_4 \cdot 10H_2O$	322.2	0.5	85.6	
Sodium sulphite, $Na_2SO_3 \cdot 7H_2O$	252.2	0.5	63.0	
Sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$ (saturated solution)	381.4	0.14	26.5	
Sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$	248.2	0.5	62.0	
Stannic chloride, $SnCl_4 \cdot 5H_2O$	350.6	0.5	43.8	
Stannous chloride $SnCl_2 \cdot 2H_2O$	225.6	0.5	56.4	Dissolved in presence of HCl .
Strontium nitrate, $Sr(NO_3)_2$	211.6	0.5	52.9	
Zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$	297.5	0.5	74.4	

E. Special Reagents

Name of reagent	Preparation
Alizarin	Saturated solution in 95% alcohol
Aluminon	Dissolve 1 g in 1 litre of water
Ammoniacal $AgNO_3$ solution (test for Cl^-)	Dissolve 1.7 g $AgNO_3$, 25 g KNO_3 and 17 ml of concentrated NH_4OH in water, dilute to 1 litre
Ammonium molybdate reagent	Dissolve 150 g of commercial ammonium molybdate in 1 litre of distilled water and pour the solution into 1 litre of HNO_3, sp. gr. 1.2 (*not the acid into the solution*). White molybdic acid is precipitated and then redissolves. Leave to stand for 48 hours and decant from any precipitate formed
Ammonium tetrathiocyanomercurate	Dissolve 8 g $HgCl_2$ and 9 g NH_4CNS in 100 ml of water

Cont'ed

Name of reagent	Preparation
Aniline hydrochloride	Mix equal volumes of aniline and concentrated HCl (sp. gr. 1.19)
Benzidine	Saturated solution in 30% acetic acid
Bromine water	Saturated aqueous solution of bromine
Chromotropic acid	5% aqueous solution
Cobalt chloride (test for Zn^{++})	0.02% solution in 0.5 *N* HCl
Dimethylglyoxime (Chugaev's reagent)	Dissolve 10 g in 1 litre of 95% alcohol (1% ammoniacal solution of dimethylglyoxime may also be used)
Diphenylamine	Dissolve 1 g in 100 ml of concentrated H_2SO_4 (sp. gr. 1.84)
Diphenylcarbazide	Dissolve 1 g in 100 ml of 95% alcohol
Dipicrylamine	Heat 10 g of the substance with 100 ml of 1 *N* Na_2CO_3 to boiling and dilute to 1 litre. Cool and filter
Dithizone	Dissolve 0.01 g in 100 ml of CCl_4 or $CHCl_3$
Fuchsin	0.1% aqueous solution
Formate buffer mixture	Mix 100 ml of concentrated (23 *N*) formic acid with 3.2 ml of concentrated (13 *N*) NH_4OH
Glycerol (glycerin)	Mix glycerin with an equal volume of water
Hydrogen peroxide (3% solution)	Dilute 10 ml of 30% H_2O_2 with water to 100 ml
Hydroxyquinoline	Dissolve 2.5 g in 100 ml of 6% acetic acid
Hydroxyquinoline and potassium iodide (reagent for bismuth and antimony)	Dissolve 2 g of hydroxyquinoline in 4 ml of 12 *N* hydrochloric acid, add 80 ml of water and 4 g of KI, dilute to 100 ml
Iodine water	Dissolve 1.3 g of iodine and 3 g of KI in the minimum amount of water and dilute with water to 1 litre
Lanthanum nitrate	Dissolve 50 g of the salt in 1 litre of water
Magnesia mixture, $MgCl_2 + NH_4Cl + NH_4OH$	Dissolve 100 g of $MgCl_2 \cdot 6H_2O$ and 100 g of NH_4Cl in water, add 50 ml of concentrated NH_4OH, and dilute with water to 1 litre
Manganese chloride	Saturated solution of $MnCl_2 \cdot 4H_2O$ in concentrated HCl (sp. gr. 1.19)

Cont'ed

Name of reagent	Preparation
Molybdate-tartrate reagent (for PO_4^{---})	Dissolve 5 g of commercial ammonium molybdate in 100 ml of cold water and add to 35 ml of HNO_3 (sp. gr. 1.2). Dissolve 20 g of tartaric acid in this solution
Morin	Saturated solution in 20% alcohol
α-Naphthylamine	Boil 0.3 g of α-naphthylamine with 20 ml of water; add 150 ml of 2 *N* CH_3COOH to the colourless solution
Nessler's reagent	Dissolve 115 g of HgI_2 and 80 g of KI in sufficient water; make up to 500 ml. Add 500 ml of 6 *N* NaOH and decant the solution from any precipitate which forms on standing. Keep the stock solution in a dark place
p-Nitrobenzene-azo-resorcinol	Dissolve 0.001 g in 100 ml of 2 *N* NaOH
α-Nitroso-β-naphthol (Il'insky's reagent)	Dissolve 1 g on warming in 20 ml of water, adding 1 ml of 2 *N* NaOH; filter, and dilute the clear filtrate to 200 ml
Phosphomolybdic acid	5% aqueous solution
Potassium dihydrogen antimonate	Dissolve 22 g of KH_2SbO_4 in 1 litre of water on heating. Boil for 3-5 minutes until all the salt has dissolved. Cool the solution rapidly and add 35 ml of 6 *N* KOH. Leave overnight and filter
Reagent for K^+, $Na_2PbCu(NO_2)_6$	Dissolve 2 g of $NaNO_2$ free from potassium salts, 0.9 g of $Cu(CH_3COO)_2 \cdot H_2O$ and 1.6 g of $Pb(CH_3COO)_2 \cdot 3H_2O$ in 15 ml of distilled water previously acidified with 0.2 ml of 30% CH_3COOH. The solution should be frequently renewed and kept in a bottle with a ground glass stopper
Rhodamine B	Dissolve 0.01 g in 100 ml of water
Sodium cobaltinitrite	Dissolve 21 g of C. P. $NaNO_2$ and 29 g of $Co(NO_3)_2 \cdot 6H_2O$ in 50 ml of distilled water, and acidify with 1 ml of 80% CH_3COOH. Leave to stand for at least 24 hours. Filter and dilute with water to 100 ml

Cont'ed

Name of reagent	Preparation
Sodium nitroprusside	Dissolve 3 g in 100 ml of water
Sodium sulphide (group reagent for cation Group V)	Dissolve 480 g of $Na_2S \cdot 9H_2O$ and 40 g of NaOH in 1 litre of water
Sodium tungstate	Heat 50 g of tungstic acid with 200 ml of 2 *N* NaOH to boiling. When dissolved, dilute to 1.5 litres
Sodium vanadate	Boil 100 g of ammonium vanadate, NH_4VO_3, with 200 ml of 2 *N* NaOH. Cool and dilute with water to 7 litres
Starch solution	Make 1 g of starch into a thin paste with a small amount of cold water, pour into 100 ml of boiling water, boil for a few minutes, and cool
Sulphanilic acid	Dissolve 0.5 g in 150 ml of 2 *N* acetic acid
Titanium (IV) sulphate	Fuse 10 g of TiO_2 with 60 g of $KHSO_4$. Pour concentrated H_2SO_4 (sp. gr. 1.84) over the cooled melt and leach with water. Dilute the solution to 2 litres
Uranyl acetate	Saturated solution in 30% CH_3COOH
Zinc uranyl acetate	(a) Dissolve 10 g of uranyl acetate, $UO_2(CH_3COO)_2 \cdot 2H_2O$, and 6 g of 30% acetic acid in 50 ml of distilled water (b) Dissolve 30 g of zinc acetate, $Zn(CH_3COO)_2 \cdot 2H_2O$, and 3 g of 30% acetic acid in 50 ml of distilled water. Mix the two solutions, leave overnight, and decant from the precipitate which forms
Zirconyl nitrate (reagent for F^-)	Dissolve 0.1 g in 20 ml of concentrated HCl and dilute to 100 ml

II. Degrees of dissociation of acids, bases and salts in aqueous solutions at 18°*

Electrolyte	Formula	Degree of dissociation %	
		in 1 *N* solutions	in 0.1 *N* solutions
1. Acids			
Nitric	HNO_3	82	92
Hydrochloric	HCl	78	91

Cont'ed

Electrolyte	Formula	Degree of dissociation %	
		in 1 *N* solutions	in 0.1 *N* solutions
Hydrobromic	HBr	—	90
Hydriodic	HI	—	90
Sulphuric	H_2SO_4	51	58 **
Oxalic	$H_2C_2O_4$	—	31
Phosphoric	H_3PO_4	—	26
Sulphurous	H_2SO_3	—	20
Hydrofluoric	HF	—	15
Tartaric	$H_2C_4H_4O_6$	—	13
Acetic	CH_3COOH	0.4	1.3
Carbonic	H_2CO_3	—	0.17
Hydrogen sulphide	H_2S	—	0.07
Boric	H_3BO_3	—	0.01
Hydrocyanic	HCN	—	0.007
2. Bases			
Caustic potash	KOH	77	89
Caustic soda	NaOH	73	84
Ammonia	NH_4OH	0.4	1.3
3. Salts			
Type Me^+A^-; e. g., KCl, $NaNO_3$	—	— ***	86
Type $Me_2^+A^{--}$ or $Me^{++}A_2^-$; e. g., K_2SO_4, $BaCl_2$	—	—	73
Type $Me_3^+A^{---}$ or $Me^{+++}A_3^-$; e. g., $K_3[Fe(CN)_6]$, $AlCl_3$	—	—	65
Type $Me^{++}A^{--}$; e. g., $CuSO_4$	—	—	40

* The values given for strong electrolytes are "apparent degrees of dissociation", found from conductivity data (Sec. 13).

** The values for di- and polybasic acids refer to the first dissociation stage.

*** The apparent degrees of dissociation of 1 *N* solutions of salts of the same type differ quite considerably. Therefore they are not given in the table. The values for some salts are: KCl, 75%; NaCl, 67%; CH_3COONa, 53%; Na_2SO_4, 45%; etc.

III. Dissociation constants and exponents (pK) of some weak electrolytes

Electrolyte	Dissociation constant K	$pK = -\log K$
	ACIDS	
	Inorganic	
Arsenic, H_3AsO_4		
1st stage	5.62×10^{-3}	2.25
2nd stage	1.70×10^{-7}	6.77
3rd stage	2.95×10^{-12}	11.53
Arsenious, H_3AsO_3		
1st stage	5.8×10^{-10}	9.24
2nd stage	3×10^{-14}	13.52
Boric, H_3BO_3		
1st stage	5.70×10^{-10}	9.24
Carbonic, H_2CO_3		
1st stage	4.31×10^{-7}	6.37
2nd stage	5.61×10^{-11}	10.25
Chromic, H_2CrO_4		
1st stage	1.8×10^{-1}	0.75
2nd stage	3.2×10^{-7}	6.50
Hydrocyanic, HCN	7.2×10^{-10}	9.14
Hydrofluoric, H_2F_2	7.4×10^{-4}	3.13
Hydrogen peroxide, H_2O_2	2.4×10^{-12}	11.62
Hydrogen sulphide, H_2S		
1st stage	5.7×10^{-8}	7.24
2nd stage	1.2×10^{-15}	14.92
Iodic, HIO_3	1.67×10^{-1}	0.78
Nitrous, HNO_2	4×10^{-4}	3.40
Orthophosphoric, H_3PO_4		
1st stage	7.51×10^{-3}	2.12
2nd stage	6.23×10^{-8}	7.21
3rd stage	2.2×10^{-13}	12.67
Sulphurous, H_2SO_3		
1st stage	1.30×10^{-2}	1.89
2nd stage	5×10^{-6}	5.30
Water, H_2O	1.8×10^{-16}	15.74
	Organic	
Acetic, CH_3COOH	1.86×10^{-5}	4.73
Citric, $H_3C_6H_5O_7$		
1st stage	8.4×10^{-4}	3.08

Cont'ed

Electrolyte	Dissociation constant K	$pK = -\log K$
	ACIDS	
	Organic	
2nd stage	1.8×10^{-5}	4.74
3rd stage	4×10^{-6}	5.40
Formic, HCOOH	1.77×10^{-4}	3.75
Oxalic, $H_2C_2O_4$		
1st stage	5.9×10^{-2}	1.23
2nd stage	6.4×10^{-5}	4.19
Succinic, $H_2C_4H_4O_4$		
1st stage	6.9×10^{-5}	4.16
2nd stage	2.5×10^{-6}	5.61
Tartaric, $H_2C_4H_4O_6$		
1st stage	1.04×10^{-3}	2.98
2nd stage	4.55×10^{-5}	4.34
	BASES	
	Inorganic	
Ammonia, NH_4OH	1.79×10^{-5}	4.75
Barium hydroxide, $Ba(OH)_2$		
2nd stage	2.3×10^{-1}	0.64
Calcium hydroxide, $Ca(OH)_2$		
2nd stage	3×10^{-2}	1.50
Lead hydroxide, $Pb(OH)_2$		
1st stage	9.6×10^{-4}	3.02
2nd stage	3×10^{-8}	7.52
Water, H_2O	1.8×10^{-16}	15.74
	Organic	
Aniline, $C_6H_5NH_2$	4.0×10^{-10}	9.40
Benzidine, $(NH_2C_6H_4)_2$		
1st stage	9.3×10^{-10}	9.03
2nd stage	5.6×10^{-11}	10.25
Ethylamine, $C_2H_5NH_2$	5.6×10^{-4}	3.25
Pyridine, C_5H_5N	2.04×10^{-9}	8.69
Quinoline, C_9H_7N	1×10^{-9}	9.00

IV. Solubilities and solubility products of certain sparingly soluble electrolytes at room temperature

Formula of electrolyte	Ionic product	Numerical values	
		solubility product (*SP*)	solubility (mole/litre)
Hydroxides			
AgOH	$[Ag^+] \times [OH^-]$	2×10^{-8}	1.4×10^{-4}
$Al(OH)_3$	$[Al^{+++}] \times [OH^-]^3$	1.9×10^{-33}	2.9×10^{-9}
$Cd(OH)_2$	$[Cd^{++}] \times [OH^-]^2$	1.2×10^{-14}	1.4×10^{-5}
$Cr(OH)_3$	$[Cr^{+++}] \times [OH^-]^3$	5.4×10^{-31}	1.2×10^{-8}
$Cu(OH)_2$	$[Cu^{++}] \times [OH^-]^2$	5.6×10^{-20}	2.4×10^{-7}
$Fe(OH)_2$	$[Fe^{++}] \times [OH^-]^2$	4.8×10^{-16}	4.9×10^{-6}
$Fe(OH)_3$	$[Fe^{+++}] \times [OH^-]^3$	3.8×10^{-38}	1.9×10^{-10}
$Mg(OH)_2$	$[Mg^{++}] \times [OH^-]^2$	5×10^{-12}	1.1×10^{-4}
$Mn(OH)_2$	$[Mn^{++}] \times [OH^-]^2$	4×10^{-14}	2.1×10^{-5}
$Ni(OH)_2$	$[Ni^{++}] \times [OH^-]^2$	6.3×10^{-16}	5.4×10^{-6}
$Co(OH)_2$	$[Co^{++}] \times [OH^-]^2$	2.0×10^{-16}	3.7×10^{-6}
$Sb(OH)_3$	$[Sb^{+++}] \times [OH]^3$	4×10^{-42}	2×10^{-11}
$Sn(OH)_2$	$[Sn^{++}] \times [OH^-]^2$	5×10^{-26}	2.3×10^{-9}
$Zn(OH)_2$	$[Zn^{++}] \times [OH^-]^2$	1×10^{-17}	1.4×10^{-6}
Sulphides			
Ag_2S	$[Ag^+]^2 \times [S^{--}]$	1.6×10^{-49}	3.5×10^{-17}
Bi_2S_3	$[Bi^{+++}]^2 \times [S^{--}]^3$	1.6×10^{-72}	1.7×10^{-15}
CdS	$[Cd^{++}] \times [S^{--}]$	3.6×10^{-29}	6×10^{-15}
CoS_α	$[Co^{++}] \times [S^{--}]$	7×10^{-23}	8.4×10^{-12}
CoS_β	$[Co^{++}] \times [S^{--}]$	2×10^{-27}	4.5×10^{-14}
CuS	$[Cu^{++}] \times [S^{--}]$	8.5×10^{-45}	9.2×10^{-23}
Cu_2S	$[Cu^+]^2 \times [S^{--}]$	2.6×10^{-49}	4.1×10^{-27}
FeS	$[Fe^{++}] \times [S^{--}]$	3.7×10^{-19}	6.1×10^{-10}
HgS	$[Hg^{++}] \times [S^{--}]$	4×10^{-53}	6.3×10^{-27}
MnS	$[Mn^{++}] \times [S^{--}]$	1.4×10^{-15}	3.7×10^{-8}
PbS	$[Pb^{++}] \times [S^{--}]$	1.1×10^{-29}	3.3×10^{-15}
SnS	$[Sn^{++}] \times [S^{--}]$	1.0×10^{-28}	1.0×10^{-14}
NiS_α	$[Ni^{++}] \times [S^{--}]$	3×10^{-21}	5.5×10^{-11}
NiS_γ	$[Ni^{++}] \times [S^{--}]$	2×10^{-28}	1.4×10^{-14}
ZnS	$[Zn^{++}] \times [S^{--}]$	1.2×10^{-23}	3.5×10^{-12}
Chlorides			
AgCl	$[Ag^+] \times [Cl^-]$	1.6×10^{-10}	1.2×10^{-5}
Hg_2Cl_2	$[Hg_2^{++}] \times [Cl^-]^2$	1.1×10^{-18}	6.5×10^{-7}
$PbCl_2$	$[Pb^{++}] \times [Cl^-]^2$	2.4×10^{-4}	3.9×10^{-2}

Contd.

Formula of electrolyte	Ionic product	Numerical values	
		solubility product (S.P.)	solubility (mole/litre)
Bromides			
$AgBr$	$[Ag^+] \times [Br^-]$	7.7×10^{-13}	8.8×10^{-7}
Hg_2Br_2	$[Hg_2^{++}] \times [Br^-]^2$	5.2×10^{-23}	2.8×10^{-8}
$PbBr_2$	$[Pb^{++}] \times [Br^-]^2$	7.4×10^{-5}	2.6×10^{-2}
Iodides			
AgI	$[Ag^+] \times [I^-]$	1.3×10^{-16}	1.1×10^{-8}
Hg_2I_2	$[Hg_2^{++}] \times [I^-]^2$	4.5×10^{-29}	2.2×10^{-10}
PbI_2	$[Pb^{++}] \times [I^-]^2$	8.7×10^{-9}	1.3×10^{-3}
CuI	$[Cu^+] \times [I^-]$	1.1×10^{-12}	1.05×10^{-6}
Sulphates			
Ag_2SO_4	$[Ag^+]^2 \times [SO_4^{--}]$	7.7×10^{-5}	2.6×10^{-2}
$BaSO_4$	$[Ba^{++}] \times [SO_4^{--}]$	1.1×10^{-10}	1.05×10^{-5}
$CaSO_4 \times 2H_2O$	$[Ca^{++}] \times [SO_4^{--}]$	6.1×10^{-5}	7.8×10^{-3}
$PbSO_4$	$[Pb^{++}] \times [SO_4^{--}]$	2.2×10^{-8}	1.5×10^{-4}
$SrSO_4$	$[Sr^{++}] \times [SO_4^{--}]$	2.8×10^{-7}	5.3×10^{-4}
Hg_2SO_4	$[Hg_2^{++}] \times [SO_4^{--}]$	6.3×10^{-7}	7.9×10^{-4}
Carbonates			
Ag_2CO_3	$[Ag^+]^2 \times [CO_3^{--}]$	6.1×10^{-12}	1.15×10^{-4}
$BaCO_3$	$[Ba^{++}] \times [CO_3^{--}]$	8×10^{-9}	8.9×10^{-5}
$CaCO_3$	$[Ca^{++}] \times [CO_3^{--}]$	4.8×10^{-9}	6.9×10^{-5}
$MgCO_3$	$[Mg^{++}] \times [CO_3^{--}]$	1.0×10^{-5}	3.2×10^{-3}
$SrCO_3$	$[Sr^{++}] \times [CO_3^{--}]$	1.6×10^{-9}	4×10^{-5}
$CdCO_3$	$[Cd^{++}] \times [CO_3^{--}]$	2.5×10^{-14}	1.5×10^{-7}
$PbCO_3$	$[Pb^{++}] \times [CO_3^{--}]$	1.5×10^{-13}	3.9×10^{-7}
Oxalates			
$BaC_2O_4 \times 2H_2O$	$[Ba^{++}] \times [C_2O_4^{--}]$	1.6×10^{-7}	4×10^{-4}
$CaC_2O_4 \times H_2O$	$[Ca^{++}] \times [C_2O_4^{--}]$	2.6×10^{-9}	5.1×10^{-5}
MgC_2O_4	$[Mg^{++}] \times [C_2O_4^{--}]$	8.6×10^{-5}	9.1×10^{-3}
PbC_2O_4	$[Pb^{++}] \times [C_2O_4^{--}]$	3.2×10^{-11}	5.6×10^{-6}
$SrC_2O_4 \times H_2O$	$[Sr^{++}] \times [C_2O_4^{--}]$	5.6×10^{-8}	2.4×10^{-4}
ZnC_2O_4	$[Zn^{++}] \times [C_2O_4^{--}]$	7.5×10^{-9}	8.7×10^{-5}
Chromates			
Ag_2CrO_4	$[Ag^+]^2 \times [CrO_4^{--}]$	9×10^{-12}	1.3×10^{-4}
$BaCrO_4$	$[Ba^{++}] \times [CrO_4^{--}]$	2.4×10^{-10}	1.5×10^{-5}
$PbCrO_4$	$[Pb^{++}] \times [CrO_4^{--}]$	1.8×10^{-14}	1.3×10^{-7}
$SrCrO_4$	$[Sr^{++}] \times [CrO_4^{--}]$	3.5×10^{-5}	5.4×10^{-3}

Cont'ed

Formula of electrolyte	Ionic product	Numerical values	
		solubility product (*SP*)	solubility (mole/litre)
Phosphates			
Ag_3PO_4	$[Ag^+]^3 \times [PO_4^{---}]$	1.8×10^{-18}	1.6×10^{-5}
$MgNH_4PO_4$	$[Mg^{++}] \times [NH_4^+] \times [PO_4^{---}]$	2.5×10^{-13}	6.3×10^{-5}
$Pb_3(PO_4)_2$	$[Pb^{++}]^3 \times [PO_4^{---}]^2$	1.5×10^{-32}	1.7×10^{-7}
Salts of various acids			
$AgBrO_3$	$[Ag^+] \times [BrO_3^-]$	5.8×10^{-5}	7.6×10^{-3}
AgCNS	$[Ag^+] \times [CNS^-]$	1.16×10^{-12}	1.1×10^{-6}
Salts of various acids			
$Ag_4[Fe(CN)_6]$	$[Ag^+]^4 \times [Fe(CN)_6^{=}]$	1.5×10^{-41}	2.2×10^{-9}
$Ag_3[Fe(CN)_6]$	$[Ag^+]^3 \times [Fe(CN)_6^{---}]$	9.8×10^{-26}	2.4×10^{-7}
Ag_3AsO_3	$[Ag^+]^3 \times [AsO_3^{---}]$	4.5×10^{-19}	1.1×10^{-5}
Ag_3AsO_4	$[Ag^+]^3 \times [AsO_4^{---}]$	1.0×10^{-19}	7.8×10^{-6}
CaF_2	$[Ca^{++}] \times [F^-]^2$	4×10^{-11}	2.1×10^{-4}
$KHC_4H_4O_6$	$[K^+] \times [HC_4H_4O_6^-]$	3×10^{-4}	1.7×10^{-2}

V. Instability constants of certain complexes

Complex-former	Equation for dissociation of complex	Instability constant K_{inst}	$pK_{inst} = -\log K_{inst}$
Ag^+	$[Ag(NH_3)_2]^+ \rightleftarrows Ag^+ + 2NH_3$	6.8×10^{-8}	7.2
	$[AgS_2O_3]^- \rightleftarrows Ag^+ + S_2O_3^{--}$	1×10^{-13}	13.0
	$[Ag(CN)_2]^- \rightleftarrows Ag^+ + 2CN^-$	1×10^{-21}	21.0
Al^{+++}	$[AlF_6]^{---} \rightleftarrows Al^{+++} + 6F^-$	2×10^{-24}	23.7
Cd^{++}	$[Cd(NH_3)_4]^{++} \rightleftarrows Cd^{++} + 4NH_3$	1×10^{-7}	7.0
	$[CdCl_4]^{--} \rightleftarrows Cd^{++} + 4Cl^-$	9×10^{-3}	2.05
	$[Cd(CN)]_4^{--} \rightleftarrows Cd^{++} + 4CN^-$	1.4×10^{-17}	16.85

Cont'ed

Complex-former	Equation for dissociation of complex	Instability constant K_{inst}	$pK_{inst} = -\log K_{inst}$
Co^{++}	$[Co(NH_3)_6]^{++} \rightleftarrows Co^{++} + 6NH_3$	1.25×10^{-5}	4.91
	$[Co(CNS)_4]^{--} \rightleftarrows Co^{++} + 4CNS^-$	1×10^{-3}	3.0
Co^{++}	$[Co(NH_3)_6]^{+++} \rightleftarrows Co^{+++} + 6NH_3$	6×10^{-36}	35.22
Cu^{++}	$[Cu(NH_3)_4]^{++} \rightleftarrows Cu^{++} + 4NH_3$	4.6×10^{-14}	13.34
Cu^{+}	$[Cu(CN)_4]^{---} \rightleftarrows Cu^{+} + 4CN^-$	5×10^{-28}	27.30
Fe^{++}	$[Fe(CN)_6]^{====} \rightleftarrows Fe^{++} + 6CN^-$	5×10^{-37}	36.30
Fe^{+++}	$[Fe(CN)_6]^{---} \rightleftarrows Fe^{+++} + 6CN^-$	5×10^{-44}	43.30
Hg^{++}	$[Hg(CNS)_4]^{--} \rightleftarrows Hg^{++} + 4CNS^-$	1×10^{-22}	22.0
	$[HgCl_4]^{--} \rightleftarrows Hg^{++} + 4Cl^-$	6×10^{-17}	16.22
	$[HgI_4]^{--} \rightleftarrows Hg^{++} + 4I^-$	5×10^{-31}	30.30
Ni^{++}	$[Ni(NH_3)_6]^{--} \rightleftarrows Ni^{++} + 6NH_3$	6×10^{-9}	8.22
	$[Ni(CN)_4]^{--} \rightleftarrows Ni^{++} + 4CN^-$	3×10^{-16}	15.52
Sn^{++++}	$[SnCl_6]^{---} \rightleftarrows Sn^{++++} + 6Cl^-$	1.5×10^{-1}	0.82
Zn^{++}	$[Zn(NH_3)_4]^{++} \rightleftarrows Zn^{++} + 4NH_3$	3.5×10^{-10}	9.46
	$[Zn(CN_4)]^{--} \rightleftarrows Zn^{++} + 4CN^-$	2×10^{-17}	16.70
	$[Zn(C_2O_4)_3]^{====} \rightleftarrows Zn^{++} + 3C_2O_4^{--}$	1×10^{-9}	9.0

VI. Preparation of Buffer Mixtures

pH	Method of preparation
0	1.3 *N* hydrochloric acid (corrected for activity coefficient)
1	Add 0.75 g KCl to 194 ml of 0.1 *N* HCl and dilute with water to 200 ml
2	Add 0.75 g KCl to 21.2 ml of 0.1 *N* HCl and dilute with water to 200 ml
3	Mix 102.75 ml of 0.2 *M* sodium phosphate, ($Na_2HPO_4 \cdot 2H_2O$), with 397.25 ml of 0.1 *M* citric acid, $C_6H_8O_7 \cdot H_2O$

Cont'ed

pH	Method of preparation
4	Mix 192.75 ml of 0.2 *M* $Na_2HPO_4 \cdot 2H_2O$ with 307.25 ml of 0.1 *M* citric acid, $C_6H_8O_7 \cdot H_2O$
5	Mix 257.5 ml of 0.2 *M* $Na_2HPO_4 \cdot 2H_2O$ with 292.5 ml of 0.1 *M* citric acid, $C_6H_8O_7 \cdot H_2O$
6	Mix 315.75 ml of 0.2 *M* $Na_2HPO_4 \cdot 2H_2O$ with 184.25 ml of 0.1 *M* citric acid, $C_6H_8O_7 \cdot H_2O$
7	Mix 411.75 ml of 0.2 *M* $Na_2HPO_4 \cdot 2H_2O$ with 88.25 ml of 0.1 *M* citric acid, $C_6H_8O_7 \cdot H_2O$
8	Mix 483.25 ml of 0.2 *M* $Na_2HPO_4 \cdot 2H_2O$ with 13.75 ml of 0.1 *M* citric acid, $C_6H_8O_7 \cdot H_2O$
9	Mix 106.5 ml of 0.1 *M* NaOH with 250 ml of 0.1 *M* boric acid solution
10	Mix 219.5 ml of 0.1 *M* NaOH with 250 ml of 0.1 *M* boric acid solution in 0.1 *N* KCl
11	Mix 120 ml of 0.1 *M* NaOH with 400 ml of 0.15 *M* $Na_2HPO_4 \cdot 2H_2O$
12	Mix 300 ml of 0.1 *M* NaOH with 200 ml of 0.15 *M* $Na_2HPO_4 \cdot 2H_2O$
13	0.1 *M* NaOH

VII. Indicators for pH determination

Indicator	Range	Colour*		Preparation of indicator solution
		acid form	alkaline form	
Methyl violet**	0-2	Green	Violet	0.042 g of indicator dissolved in 100 ml of water
Thymol blue	1.2-2.8	Red	Yellow	0.2 g of indicator dissolved in 100 ml of 50% ethyl alcohol
Ditto	8.0-9.6	Yellow	Blue	
Methyl orange	3.1-4.4	Pink	Orange-yellow	0.035 g of indicator dissolved in 100 ml of water

Cont'ed

Indicator	Range	Colour*		Preparation of indicator solution
		acid form	alkaline form	
Methyl red	4.4-6.2	Red	Yellow	0.1 g of indicator dissolved in 100 ml of ethyl alcohol
Phenol red	6.8-8.0	Yellow	Red	0.1 g of indicator dissolved in 100 ml of 25% ethyl alcohol
Phenolphthalein	8.0-10.0	Colourless	Red	0.1 g of indicator dissolved in 100 ml of ethyl alcohol
Thymolphthalein	9.3-10.5	Colourless	Blue	0.5 g of indicator dissolved in 100 ml of ethyl alcohol
Kolthoff's universal indicator	2.0-10.0	See p. 82	See p. 82	Following volumes of 0.1% alcoholic solutions of different indicators are mixed: (a) 15 ml of dimethylaminoazobenzene; (b) 20 ml of bromthymol blue; (c) 5 ml of methyl red; (d) 20 ml of phenolphthalein; (e) 20 ml of thymolphthalein ***

* The colour of the acid form is observed at and below the bottom limit of the range; the colour of the alkaline form, at and above the top limit.

** Methyl violet is blue at pH = 1.

*** A prepared mixture of these indicators in powdered form is commercially available under the name of ZIV1. An ampoule contains 0.16 g of the mixture; the contents should be dissolved in 100 ml of 80% ethyl alcohol. See also p. 82 with reference to the universal indicator paper marketed by the Riga Laboratory of the D. I. Mendeleyev All-Union Chemical Society.

VIII. Standard oxidation potentials

Symbols: (g) = gas; (liq) = liquid; (s) = solid

Reduced form	Number of electrons	Oxidized form	Potential E_0 in volts
Li (s)	1*e*	Li^+	−2.96
K (s)	1*e*	K^+	−2.92
Ca (s)	2*e*	Ca^{++}	−2.76
Na (s)	1*e*	Na^+	−2.71
Mg (s)	2*e*	Mg^{++}	−2.34
Al (s)	3*e*	Al^{+++}	−1.30
Mn (s)	2*e*	Mn^{++}	−1.10
Zn (s)	2*e*	Zn^{++}	−0.76
S^{--}	2*e*	S (s)	−0.51
Fe (s)	2*e*	Fe^{++}	−0.44
Cr^{++}	1*e*	Cr^{+++}	−0.41
Cd (s)	2*e*	Cd^{++}	−0.40
Ni (s)	2*e*	Ni^{++}	−0.23
Sn (s)	2*e*	Sn^{++}	−0.14
Pb (s)	2*e*	Pb^{++}	−0.13
Fe (s)	3*e*	Fe^{+++}	−0.04
H_2 (g)	2*e*	$2H^+$	**0.00**
Sn (s)	4*e*	Sn^{++++}	+0.01
$2S_2O_3^{--}$	2*e*	$S_4O_6^{--}$	(+0.1)
H_2S	2*e*	S (s) + $2H^+$	+0.14
Sn^{++}	2*e*	Sn^{++++}	+0.15
Cu^+	1*e*	Cu^{++}	+0.17
Sb (s)	3*e*	Sb^{+++}	+0.20
$SO_3^{--} + H_2O$	2*e*	$SO_4^{--} + 2H^+$	+0.22
Bi (s)	3*e*	Bi^{+++}	+0.23
Cu (s)	2*e*	Cu^{++}	+0.34
Cu (s)	1*e*	Cu^+	+0.52
MnO_2 (s) + $4OH^-$	3*e*	$MnO_4^- + 2H_2O$	+0.54
$2I^-$	2*e*	I_2 (s)	+0.54
$AsO_3^{---} + H_2O$	2*e*	$AsO_4^{---} + 2H^+$	+0.57
MnO_4^{--}	1*e*	MnO_4^-	+0.66
H_2O_2	2*e*	O_2 (g) + $2H^+$	+0.68
Fe^{++}	1*e*	Fe^{+++}	+0.77
NO_2 (g) + H_2O	1*e*	$NO_3^- + 2H^+$	+0.77
Ag (s)	1*e*	Ag^+	+0.80
Hg (liq)	2*e*	Hg^{++}	+0.86
$NH_4^+ + 3H_2O$	8*e*	$NO_3^- + 10H^+$	+0.87
NO (g) + $2H_2O$	3*e*	$NO_3^- + 4H^+$	+0.95

Cont'ed

Reduced form	Number of electrons	Oxidized form	Potential E_0 in volts
$NO\ (g)+H_2O$	1*e*	HNO_2+H^+	+0.98
$2Br^-$	2*e*	$Br_2\ (liq)$	+1.07
I^-+3H_2O	6*e*	$IO_3^-+6H^+$	+1.08
$I_2\ (s)+6H_2O$	10*e*	$2IO_3^-+12H^+$	+1.20
$2H_2O$	4*e*	$O_2\ (g)+4H^+$	+1.23
$Mn^{++}+2H_2O$	2*e*	$MnO_2\ (s)+4H^+$	+1.24
$Au\ (s)$	3*e*	Au^{+++}	+1.29
Br^-+H_2O	2*e*	$HBrO+H^+$	+1.35
$2Cl^-$	2*e*	$Cl_2\ (g)$	+1.36
$2Cr^{+++}+7H_2O$	6*e*	$Cr_2O_7^{--}+14H^+$	+1.36
Cl^-+3H_2O	6*e*	$ClO_3^-+6H^+$	+1.44
$Pb^{++}+2H_2O$	2*e*	$PbO_2\ (s)+4H^+$	+1.46
$Au\ (s)$	1*e*	Au^+	+1.50
$Mn^{++}+4H_2O$	5*e*	$MnO_4^-+8H^+$	+1.51
$2H_2O$	2*e*	$H_2O_2+2H^+$	+1.80
$Bi^{+++}+Na^++3H_2O$	2*e*	$NaBiO_3\ (s)+6H^+$	> +1.80
Co^{++}	1*e*	Co^{+++}	+1.84
$2SO_4^{--}$	2*e*	$S_2O_8^{--}$	+2.05
$O_2\ (g)+H_2O$	2*e*	$O_3\ (g)+2H^+$	+2.07
$2F^-$	2*e*	$F_2\ (g)$	+2.85

IX. Atomic weights of certain elements

Element	Symbol	Atomic weight	Element	Symbol	Atomic weight
Aluminium	Al	26.98	Chlorine	Cl	35.457
Antimony	Sb	121.76	Chromium	Cr	52.01
Arsenic	As	74.91	Cobalt	Co	58.94
Barium	Ba	137.36	Copper	Cu	63.54
Bismuth	Bi	209.00	Fluorine	F	19.00
Boron	B	10.82	Gold	Au	197.0
Bromine	Br	79.916	Hydrogen	H	1.0080
Cadmium	Cd	112.41	Iodine	I	126.91
Caesium	Cs	132.91	Iron	Fe	55.85
Calcium	Ca	40.08	Lead	Pb	207.21
Carbon	C	12.011	Lithium	Li	6.940

Cont'ed

Element	Symbol	Atomic weight	Element	Symbol	Atomic weight
Magnesium	Mg	24.32	Selenium	Se	78.96
Manganese	Mn	54.94	Silicon	Si	28.09
Mercury	Hg	200.61	Silver	Ag	107.880
Molybdenum	Mo	95.95	Sodium	Na	22.991
Nickel	Ni	58.71	Strontium	Sr	87.63
Nitrogen	N	14.008	Sulphur	S	32.066
Oxygen	O	16	Tin	Sn	118.70
Palladium	Pd	106.4	Titanium	Ti	47.90
Phosphorus	P	30.975	Tungsten	W	183.86
Platinum	Pt	195.09	Uranium	U	238.07
Potassium	K	39.100	Vanadium	V	50.95
Radium	Ra	226.05	Zinc	Zn	65.38

NAME INDEX

Akhmatov, P. N., 19
Aksel'rud, N. V., 127
Alimarin, I. P., 238
Arrhenius, S., 40, 49, 51, 54, 61, 62

Babko, A. K., 187, 228, 421, 422
Bakh, A. N., 40, 337
Belyankin, D. S., 19
Bergman, T. O., 36
Berzelius, J. J., 38
Beskov, S. D., 412
Blok, N. I., 380
Boyle, Robert, 36, 37
Brodsky, A. I., 61
Brönsted, J. N., 147
Bunsen, R. W., 38

Chugaev, L. A., 39, 230, 239, 278
Coulomb, 221

Dalton, T., 38
Debye, P., 61

Faraday, M., 322
Fedorov, E. S., 36
Feigl, F., 40
Fialkov, Ya. A., 127
Flavitsky, F. M., 277, 284
Fresenius, K. P., 36

Gay-Lussac, J. L., 38

Hückel, E., 61

Il'insky, M. A., 39, 239, 292, 306

Kablukov, I. A., 50, 54
Kirchhoff, G. R., 38
Kistyakovsky, V. A., 50
Kolthoff, I. M., 82
Komarovsky, A. S., 515
Korabel'nik, R. K., 401
Kossel, 221
Kurnakov, N. S., 41, 230
Kuznetsov, V. I., 238

Lakomkin, I. G., 502
Lavoisier, A. L., 37
Leibig, J., 38
Lomonosov, M. V., 19, 36, 37
Lowitz, T. E., 19, 36
Lowry, 147

Mendeleyev, D. I., 33, 34, 38, 54, 228, 230, 254, 255, 258, 415
Menshutkin, N. A., 32, 38
Mizetskaya, I. B., 118

Mohr, 224-225, 230
Nernst, W., 40, 323, 324, 329
Nessler, 95, 96, 355

Orlova, L. M., 287, 525
Ostwald, W., 40

Petrashen, V. I., 413
Petrov, V. V., 38

Pisarzhevsky, L. V., 40, 240
Pleskov, V. A., 61
Poluektov, N. S., 91, 515

Raoult, 49

Sakhiev, I. S., 412
Semenchenko, V. K., 61
Severgin, V. M., 37
Shilov, N. A., 40, 337, 338
Slizkovskaya, O. A., 412

Tananaev, I. V., 118, 283
Tananaev, N. A., 40, 102, 143, 144, 257, 283, 367, 391, 413, 420, 421, 428, 515, 517, 526, 527, 528
Tsvett, M. S., 36
van't Hoff, 49

Werner, 226

SUBJECT INDEX

A

Acceptor, 229
Acetate ion, reactions, 474
Acetic acid, 474, 531
Acid-base indicators, 79
Acids, 147
  dissociation constants, 540
  dissociation, degree of, 538-539
  dissociation exponent (pK), 71, 540-541
  protolytic theory, 147
  solutions, preparation, 530-531
Activity, 63
  coefficient, 63 et seq.
  of ions, 63 et seq.
Adsorption, 14
  internal, 196
Alizarin, 267
  as reagent for Al^{+++}, 267
  as reagent for F^-, 443
  solution, preparation, 535
Alkalies, solutions, preparation, 531
Alloys, 506 et seq.
  aluminium, 507
    analysis, 512
  composition and properties, 508
  copper, 507
    analysis, 511
  iron, 506
    analysis, 510
  magnesium, 507
  lead, 509
    analysis, 513
  tin, 509
    analysis, 513
Aluminates, 264
Aluminium, alloys, 507
    analysis, 512
    reactions, 263-265, 519
Aluminon, formula, 267
    reagent for Al^{+++}, 267
    solution, preparation, 535
Ammonium ion, reactions, 94
    separation of, 97
Ammonium molybdate solution, as reagent for arsenate ion, 390
    as reagent for PO_4^{---}, 438
    solution, preparation, 535
Ammonium polysulphide, 381
Ammonium salts, solutions, preparation, 532
Ammonium sulphide, 183
Ammonium tetrathiocyanatomercurate, as reagent for Co^{++}, 293
    as reagent for Zn^{++}, 288
    solutions, preparation, 535
Amphiprotic substances, 148
Amphoteric compounds, 217
Amphoterism, 217
Amyl acetate, 474
Analysis, anion (*see* Anions)
    cation (*see* Cations)
    chemical methods, 12, 14
    chromatographic method, 14
    drop reactions (spot tests), 12, 515
    fractional, 28
    general course of, 485
    luminescence, 14
    macro, 12
    of metals and alloys, 506-514

micro, 12
microcrystalloscopic, 12
physical methods, 14
physico-chemical methods, 14
polarographic method, 15
preliminary observations, 485
preliminary tests, 486
preparation of substances for, 485
pyrochemical methods, 15-16
qualitative, defined, 11
without hydrogen sulphide, 410
quantitative, defined, 11
radioactivation method, 15
semimicro, 12
of solid substances, complete, 491-497
insoluble in acids, 495
insoluble in water, 493
soluble in water, 491
spectrum, 14
spot tests, 12, 515
systematic, 28
tracer-atom method, 15
ultramicro, 12
Analytical chemistry, 11
development of, 36-41
methods of, 11
subject of, 11
Aniline black, 420
Aniline hydrochloride, 420, 536
Antimony ions, reactions, 393-397, 528
Anions, analysis, 428 et seq.
analysis of mixtures
Cl^-, Br^- and I^-, 455
PO_4^{---}, AsO_4^{---} and AsO_3^{---}, 439
S^{--}, $S_2O_3^{--}$, SO_3^{--} and SO_4^{--}, 458
Groups I-III, 476
Group II, 466
classification, 428-429
detection, 503
Group I, analysis, 428-447
group reagent, 429
Group II, analysis, 447-468
group reagent, 447
Anions, Group III, analysis, 469-483
Aqua regia, 263, 493
Arrhenius theory of electrolytic dissociation, 15, 49, 54
Arsenate ion, reactions, 389-390
Arsenic acid, 238-239
Arsenic ions, reactions, 389, 527
Arsenite ion, reactions, 389
Atomic weights, 549-550
Aurentia (ammonium salt), 91

B

Barium ion, reactions, 163-166
Baryta water, 531
Bases, 51
dissociation constants, 541
dissociation, degrees of, 539
dissociation exponents, 541
Beads, coloured, 15, 488-489
Benzidine, formula, 273
as reagent for chromium, 273
copper, 358
lead, 353
manganese, 283
ferricyanide ion, 465
phosphate ion, 438
solution, preparation, 536
Bismuth ion, reactions, 362-366
Blank experiment, 27
Blow-pipe, 487
Bond, coordinate, 229-230
covalent, 229
donor-acceptor, 229
ionic, 226
nonionic, 226
Borate ions, reactions, 440
Boric acid, 440
Bromide ion, reactions, 451
Bromine water, preparation, 536
Brönsted-Lowry theory, 147
Buffer capacity, 77
Buffer mixtures, 73, 78
preparation, 78, 545-546

Buffer solutions (*see* Buffer mixtures)
Buffer systems, 72

C

Cadmium ion, reactions, 359-362, 526-527
Calcium ion, reactions, 168-169
Carbonate ion (CO_3^{--}), reactions, 435
Carbonic acid, 435
Catalysts, 338
Cations, classification, 32 et seq., 517
  detection, 491 et seq.
  electronic structures, 34, 343, 381
  general course of analysis, 491
    in presence of phosphate ions, 498
  Group I, 43 et seq.
    analysis of mixtures, 104
    in presence of phosphate ions, 498
    general characteristics, 85
    reactions, 85 et seq.
  Group II, 111 et seq.
    analysis of mixtures, 170
      in presence of phosphate ions, 498
    detection, in separate portions of solutions, 176
    general characteristics, 153
    group reagent, 32, 155
    reactions, 153 et seq.
  Group III, 180 et seq.
    analysis of mixtures, 296, 302
      in presence of phosphate ions, 498
    general characteristics, 256
    group reagent, 32, 258
    reactions, 256 et seq.
  Group IV, 317 et seq.
    analysis of mixtures, 366
    general characteristics, 340
    group reagent, 32, 343
    reactions, 340 et seq.
  Group V, 379 et seq.
    analysis of mixtures, 401
  Cations, Group V, general characteristics, 379
    group reagent, 32, 384
    reactions, 389 et seq.
Central ion (complex-former), 226-227
Chelate compounds, 238
Chemical equilibrium (*see also* Equilibrium), 43
Chloride ion, reactions, 447
Chromate ion, reactions, 269, 272
Chromatographic column, 502
Chromatographic method, 14, 502
Chromic mixture, 275
Chromium ions, reactions, 269, 520
Chromotropic acid, formula, 419
Chromotropic acid, as reagent for Ti^{+++}, 419
  solution, preparation, 536
Chugaev's reagent (*see* Dimethylglyoxime)
Coagulant electrolyte, 260
Coagulation, 193, 235
Cobalt chloride, as reagent for Zn^{++}, 288
  solution, preparation, 536
Cobalt ion, reactions, 290-293, 522
Collector, 198
Colloidal protection, 194
Colloidal solutions (sols), 190
Colloidal systems, 189
Colloids, lyophilic, 193
  lyophobic, 193
Common ion effect, 57
Common ions, 57
  effect on solubility, 117
Complexes, 226
  dissociation, 225-226
  instability constant, 231
  significance, in analysis, 235
  stability, 230
  structure, 226-230
Complex compounds (*see also* Complexes), 226
  structure, 226-230
Complex-former, 226

Complex salts, 226, 235
Compounds of higher order, 224-225, 230
Concentration, of solutions, 21
molar, 24
normal, 22
Constant
dissociation, 54, 56, 216, 540-541
thermodynamic, 66
equilibrium, 46
hydrolysis, 208
instability, 231, 544-545
rate, 44
reaction rate, 44
Coordinate bond, 229-230
Coordination bond, 237, 238
Coordination number, 227
Coordination sites, 237
Coordination sphere, inner, 226-227
outer, 226-227
Coordination theory, 226
Coordination-unsaturated compounds, 227-228
Copper, alloys, 507
analysis, 511
reactions, 356, 525
Coprecipitation, 195 et seq.
adsorptional, 196
isomorphous, 196
Coulomb's law, 221
Coupled oxidation, 337
Couples, oxidation-reduction, 319
Covalent bonds, 229
Cyclic (ring) structure, 238

D

Debye-Hückel theory, 61
Degree, of hydrolysis, 201, 208, 216
of ionization (*see* Dissociation)
Delayed precipitation effect, 197
Detectable minimum, 25
Dichromate ion, reactions, 269-272
Diffuse layer, 192
Dilution law, 55
Dilution limit, 25
Dimethylglyoxime, as reagent for iron, 278
as reagent for nickel, 237, 295
solution, preparation, 536
Diphenylamine, solution, preparation, 536
test for ferricyanide ion, 465
test for nitrate ion, 471
Diphenylcarbazide, solution, preparation, 536
test for mercury, 356
Diphenylthiocarbazone (*see* Dithizone)
Dipicrylamine, formula, 91
as reagent for potassium, 91
solution, preparation, 536
Dipoles, 52
Disperse phase, 189
Disperse system, 189
Dispersion medium, 189
Dissociation, constant, 54, 56,
thermodynamic, 66
degree of, 48, 56
apparent, 50
electrolytic, 17, 48 et seq.
of complexes, 226
of double salts, 224-225
of water, 67
exponent, of acids and bases, 71, 540
Dissociation, electrolytic, 17, 48
degree of, 48
apparent, 50
mechanism, of weak electrolytes, 52
Dissolution, metals and alloys, 507 et seq.
precipitates, 135
solid substances, 491 et seq.
Dithizone (diphenylthiocarbazone),
as reagent for Zn^{++}, 287
solution, preparation, 536
Donor, 229
Donor-acceptor bond, 229

Double salts, 224-225, 235
Dropping mercury cathode, 15

E

Electrical conductance, 48
  equivalent, 48-49
Electrolytes, 17, 48
  sparingly soluble, interconversion of, 139
  solubility of, 542-544
  solubility products of, 542-544
  strong, 48 et seq.
    state of, in solutions, 60
  weak, 48 et seq.
    dissociation constants, 540
    exponents, 540
Electrolytic bridge, 318
Electrolytic dissociation, theory of, 146-147
Electromotive force (emf), 242
Electronic theory of the structure of matter, 228, 240
Electron-ion method, for deriving equations for redox reactions, 247-248
Electrostatic forces, 53
Emulsion, 189
Equilibrium, chemical, 43, 45
  constant, 46
  dynamic, 45, 112
  ionic, 57
  mobile, 45
  shift of, 47
Equilibrium constant, 46
Equivalent conductance, 48
Ethyl acetate, 474
Ethyl acetate, formation of, 474
Evaporation, 98
Extraneous ions, 28

F

Faraday number, 322
Ferricyanic acid, 464
Ferricyanide ion, reactions, 464
Ferrocyanic acid, 462
Ferrocyanide ion, reactions, 462
Filter, paper, preparation, 160-161
Filters, 160-161
Filtration, 160-161
Flame test (flame colouration), 15
  barium, 166
  boron, 441
  calcium, 170
  copper, 359
  potassium, 91
  sodium, 93
  stannic hydride, 401
  strontium, 168
Flavitsky's grinding method, 16
  detection of acetate ion, 474
  cobalt, 293
  iron, 277
Flotation, 27
Fluoride ion, reactions, 441
Fluxes, 16, 507
Fuchsin, as reagent for Br^-, 452
  as reagent for SO_3^{--}, 433
  solution, preparation, 536
Fundamental equation, of the protolytic theory, 151
Fusion, 16, 495, 507

G

Galvanic cell, 241
Gas burner flame, structure of, 490
Gas chamber, 96
Gegenions, 192
Gels, 195
Glycerol, as reagent for separation of Cd^{++}, 360
  solution, preparation, 536
Gram-equivalent, 22
Group reagent, 30
  anions, Group I, 429
    Group II, 429
  cations, Group II, 32, 155
    Group III, 32, 258-263

Group reagent, 30
Group IV, 32, 343-349
Group V, 32, 384-388
Gypsum water (calcium sulphate), as reagent for Sr^{++}, 166
preparation, 534

H

Half-cells, 319
Heterogeneous systems, 111
Homogeneous systems, 111
Hydrates, 53
Hydrate theory of solutions, Mendeleyev's, 54
Hydriodic acid, 452
Hydrobromic acid, 451
Hydrochloric acid, 477, 530
Hydrofluoric acid, 441
Hydrogen ion concentration (*see* Hydrogen ion exponent)
Hydrogen ion exponent (pH), 67, 69
determination, 79
calculation, 212
for salt solutions, 208
Hydrogen sulphide, 180, 343-344
Hydrolysis, 200-217, 256
constant, 208
degree of, 201, 208, 216
Hydronium ion, 53
Hydrosulphuric acid, 456
Hydroxides, precipitation pH, 128
Hydroxyl ion exponent (pOH), 70
Hydroxyquinoline, 100
reagent for Bi^{+++}, 365
Mg^{++}, 100
antimony ions, 396
solution, preparation, 536
Il'insky's reagent, solution, preparation, 537
test for Co^{++}, 292
Indicator paper, 82
Indicators, 79-83
pH ranges, 80-81
solutions, preparation, 546-547
universal, 82
Indigo prism, 94
Instability constant, 231
Interionic forces, 61
Internally complex salts, 237
Iodide ion, reactions, 452-454
Iodine water, preparation, 536
Ionic atmosphere, 61-62
Ionic bond, 226
Ionic potential, 380
Ionic product, of sparingly soluble electrolytes, 117
of water, 68
Ionic strength, of solutions, 64-65
Ions, activity of, 63
coefficients, 65
common, 57
hydrates, 53
solvates, 53
Ionization (*see* Electrolytic dissociation)
Iron, alloys, 506-507
analysis, 510
Iron (II) ion, reactions, 277
Iron (III) ion, reactions, 275, 519

K

Kolthoff's universal indicator, 82
Kossel's theory, 221

L

Lanthanum nitrate, as reagent for acetate ion, 475
solution, preparation, 536
Law of mass action, 40, 46, 331
Lead, alloys, 509
analysis, 513
reactions, 352, 523
Ligands, 226-227
Lime water, 531
Limiting ratio, 28
Litmus, 79, 80
paper, 80
solution, 80

M

Macroanalysis, 12
Magnesia mixture, 390
reagent for arsenate ion, 390
phosphate ion, 437
solution, preparation, 536
Magnesium, alloys, 507
reactions, 99
Malachite green, 433
Manganese ion, reactions, 279, 521
Masking agents, 28, 236, 239
Mendeleyev's hydrate theory of solutions, 54
Mendeleyev's periodic system, 254, 255, 258, 341
Mercury ions, reactions, 354, 524
Metaantimonic acid, 497
Metaboric acid, 440
Metals, analysis, 506
potential series, 327
technically pure, 506
Metatitanic acid, 415
Metavanadic acid, 415
Methylene blue, 445
Methyl orange, 81, 546
Methyl red, 81, 546
Methyl violet, 81, 546
as reagent for antimony, 395
zinc, 288
Micelle, 192
Microanalysis, 12
Microcosmic salt, 15, 270, 489
Microcrystalloscopic analysis, 19
Microcrystalloscopic test, 12, 18-21
aluminium, 268
antimony, 396
arsenate, 392
arsenic, 392-393
barium, 165
bismuth, 366
cadmium, 362
calcium, 170
cobalt, 293
copper, 358-359
Microcrystalloscopic test, dichromate, 275
fluoride, 443
lead, 353
magnesium, 101
manganese, 284
mercury, 356
nickel, 296
nitrate, 471
nitrite, 474
potassium, 90
silicate, 445
silver, 351
sodium, 93
strontium, 167
tin, 400-401
zinc, 289
Microgram, 25
Microscope, 20-21
Millimicron, 189
Mohr's salt, 224-225, 230
Molybdate ion, reactions, 421
Molybdate-tartrate reagent, preparation, 537
Molybdenum, 415
Molybdenum blue, 396, 438
Morin, 268
as reagent for Al^{+++}, 268
solution, preparation, 537

N

α-Naphthylamine, formula, 473
reagent for NO_2^-, 473
solution, preparation, 537
Nernst equation, 322
Nssler's reagent, 95, 96, 98, 105, 107
solution, preparation, 537
test for NH_4^+, 95-96
Nickel ion, reactions, 294-296
Nitrate ion, reactions, 469
Nitric acid, 469, 530
Nitrite ion, reactions, 472
removal, 473
Nitron, 471

p-Nitrobenzene-azo-resorcinol, formula, 102
reagent for Mg^{++}, 102
solution, preparation, 537
o-Nitrophenylarsonic acid, 238-239
α-Nitroso-β-naphthol, formula, 292
reagent for Co^{++}, 292
solution, preparation, 537
Nitrous acid, 472
α-Nitroso-β-naphthol (*see* Il'insky's reagent)
Nonionic bond, 226

O

Occlusion, 197
Organic synthesis, 39
Orthoantimonic acid, 91
Orthoboric acid, 440
Orthophosphoric acid, 437
Orthovanadic acid, 415
Osmotic pressure, 63
Oxalate ion, reactions, 445-446
removal, 446
Oxalic acid, 445
Oxidation, 240, 242, 243, 317
Oxidation potentials, 317-324
numerical values, table, 325, 548
standard, 322, 325, 548
Oxidation-reduction couple, 319
Oxidation-reduction processes, 240
Oxidation-reduction reactions (*see* Reactions)
Oxidizing activity, 240
Oxidizing agent, 243, 317, 326 et seq.
Oxythiosalts, 387

P

Peptization effect, 195
Perchromic acid, 274
Periodic system, Mendeleyev's, 228
Permanganate ion, reactions, 475
Permanganic acid, 475
Pertitanic acid, 419
Pervanadic acid, 420
pH (*see* Hydrogen ion exponent)
Phases, in heterogeneous systems, 111
Phenolphthalein, 81, 547
Phenol red, 81, 547
Phenylarsonic acid, 238-239
Phosphate ion, reactions, 437
removal, 500
Phosphomolybdic acid, as reagent for antimony, 395
solution, preparation, 537
Phosphonic acid, 437
Physico-chemical analysis, 14
pOH, 70
Polarograph, 15
Poluektov's reagent (*see* Dipicrylamine)
Potassium ion, reactions, 86-91
Potassium dihydrogen antimonate, as reagent for Na^+, 91
solution, preparation, 537
Potassium mercuric iodide, 396
Potassium xanthate, 422
Potential series, of metals, 327
Potentials, ionic, 380
oxidation, 317, 321
standard, 322
oxidation-reduction, 321
redox, 321
Precipitates, dissolution, 135-139
formation, 122
separation, from solutions, 160
solubility, 185
washing, 162
Precipitation, with collector, 198
completeness, 29, 123
complete, test for, 158-159
complex compounds, 232
delayed, 197
fractional, 134
Group VI cations, 346
by hydrogen sulphide, 346
hydroxides, 128
practically complete, 123, 158
Protective colloids, 235

Protolytic theory, of acids and bases, 147, 149, 151
fundamental equation, 151
Proton acceptor, defined, 147
Proton donor, defined, 147
Prussian blue, 225, 276, 462
Pyrochemical methods, 15-16
Pyrovanadic acid, 415

R

Reactions, analytical, 12
antocatalytic, 339
conditions of, 24
coupled oxidation-reduction, 337-338
detection, 29
drop (*see* Spot tests)
dry-way, 15
detection of aluminium, 268
chromium, 269
cobalt, 293
manganese, 284
permanganate ion, 476
zinc, 290
equations (*see* Reaction equations)
exchange, 144
external effects in, 16
flame colouration (*see* Flame test)
forward, 43
by grinding method (*see* Flavitsky's grinding method)
ionic equations, 17
methods of carrying out, 15-18
microcrystalloscopic (*see* Microcrystalloscopic test)
oxidation-reduction, 240
influence of concentration and of reaction of medium, 329
equilibrium constants of, 332
direction of, 324
rate constant, 44
rate, 44
reverse, 43
reversible, 43-44
Reactions, selective, 28
sensitivity, 25
separation, 29
specificity of, 27-28
wet-way, 16-17, 21
Reaction equations electron-ion method for deriving, 247
for oxidation-reduction, 243
ionic, 17, 60
Reaction rate, 44
Reagents, 12
solutions, preparation, 530 et seq.
Redox potentials, 321
Reduced solubility products, 143
Reducing activity, 240
Reducing agent, 243, 317, 326 et seq.
Reduction, defined, 240, 242
Reprecipitation, 197
Rhodamine B, as reagent for antimony, 395
solution, preparation, 537
Rinmann's green, 290

S

Salt effect, 118
Salting-out, 194
Salts, basic, 86
complex, 226
degree of dissociation, 539
double, 224-225
internally complex, 237
Sedimentation, 193
Semimicroanalysis, 12
Series rule, N. A. Tananaev's, 144
Silicate ion, reactions, 443
Silver ion, reactions, 349, 523
Sodium ion, reactions, 91
Sodium cobaltinitrite, as reagent for K^+, 89
solution, preparation, 537
Sodium nitroprusside, as reagent for sulphide, 457
as reagent for sulphite, 434
solution, preparation, 538

Sodium rhodizonate, formula, 166
Sodium sulphide, as group reagent for Group V cations, 384
solution, preparation, 538
Sols (colloidal solutions), 190
Solubility, 542
influence of common ions on, 117
precipitates, 185-186
product, 113-114, 542-544
reduced, 143
Solubility product rule, 40, 134
Solutions, colloidal, 190 et seq.
preparation, 191
concentration, 21
molar, 24
normal, 22
hydrate theory of, 54
ionic strength, 64-65
normal, 22
"prepared", 504
of salts, pH calculation, 212
saturated, 112, 117
supersaturated, 117
true, 190
unsaturated, 117
Solvates, 53
Solvation, 193
Specificity, of reactions, 24, 27
of reagents, 24
Spot plates, 12, 102
Spot tests (drop reactions), 12, 515-529
aluminium, 267
antimony ion, 396
barium, 166
bismuth, 366
chromium ions, 273
Co^{++} ion, 292
copper, 356
ferrocyanide ion, 463
K^+ ion, 91
lead, 353
Mg^{++} ion, 102
manganese, 283
molybdate ion, 421
nickel, 295
Spot tests, phosphate ion, 438
silver, 351
Sr^{++} ion, 167
technique of, 518
tin ion, 399
titanium, 419
vanadate ion, 420
zinc, 287
Stabilizers, 193
Standard hydrogen electrode, 319
Standard oxidation potentials, 322, 325, 548
Stannic acids, 399
Starch, solution, preparation, 538
Starch-iodide paper, 449
Stepwise dissociation, 51-52, 202
Stepwise hydrolysis, 202-203
Stoichiometric laws, 38
Strontium ion, reactions, 166
Sulphate ion, reactions, 430
Sulphide ion, reactions, 456
Sulphides, action of acids on, 185
precipitation of, 180
solubility of, 181
Sulphite ion, reactions, 431
Sulphuric acid, 430, 530
Sulphurous acid, 431
Suspension, 189

T

Tananaev's drop reaction, 102
Tananaev's series rule, 144
Tartaric acid, 86, 531
Test for complete precipitation, 158-159
Tetraboric acid, 440
Tetraethylrhodamine (*see* Rhodamine B)
Thenard's blue, 269
Theory of galvanic cells, 40
Theory of strong electrolytes, 50, 61
Thiocyanate ion, reactions, 459
Thiocyanic acid, 459
Thiosalts, 379

Thiosulphate ion, reactions, 434
Thiosulphuric acid, 434
Thymol blue, 81, 546
Thymolphthalein, 81, 547
Tin, alloys, 509
  analysis of, 513
  reactions, 397, 527-528
Titanium, 415
Titanium ion, reactions, 418
Tungstate ion, reactions, 422
Tungsten, 416
Tungstic acid, 422
Turmeric paper, 440
Turmeric paper test, 440-441
Turnbull's blue, 278, 464

U

Ultramicroanalysis, 12
Ultraviolet rays, 14
Universal indicator, 82, 547
Uranyl acetate, as reagent for Na^+, 93
  solution, preparation, 538

V

Valency, 243, 246
Vanadate ion, reactions, 419, 420
Vanadium, 415
Voltaic cell (*see* Galvanic cell)

W

Wash bottles, 161
Washing of precipitates, 162
Water, dissociation, 67
  distilled, 83
  ionic product, 68
Werner's theory, 226

Z

Zinc, reactions, 285, 526
Zinc uranyl acetate, as reagent for Na^+, 92
  solution, preparation, 538
Zirconyl nitrate, as reagent for F^-, 443
  solution, preparation, 538